THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. LII APRIL 1957 No. 4

Published Monthly by

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LII APRIL 1957 No. 4

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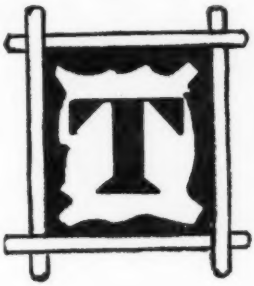

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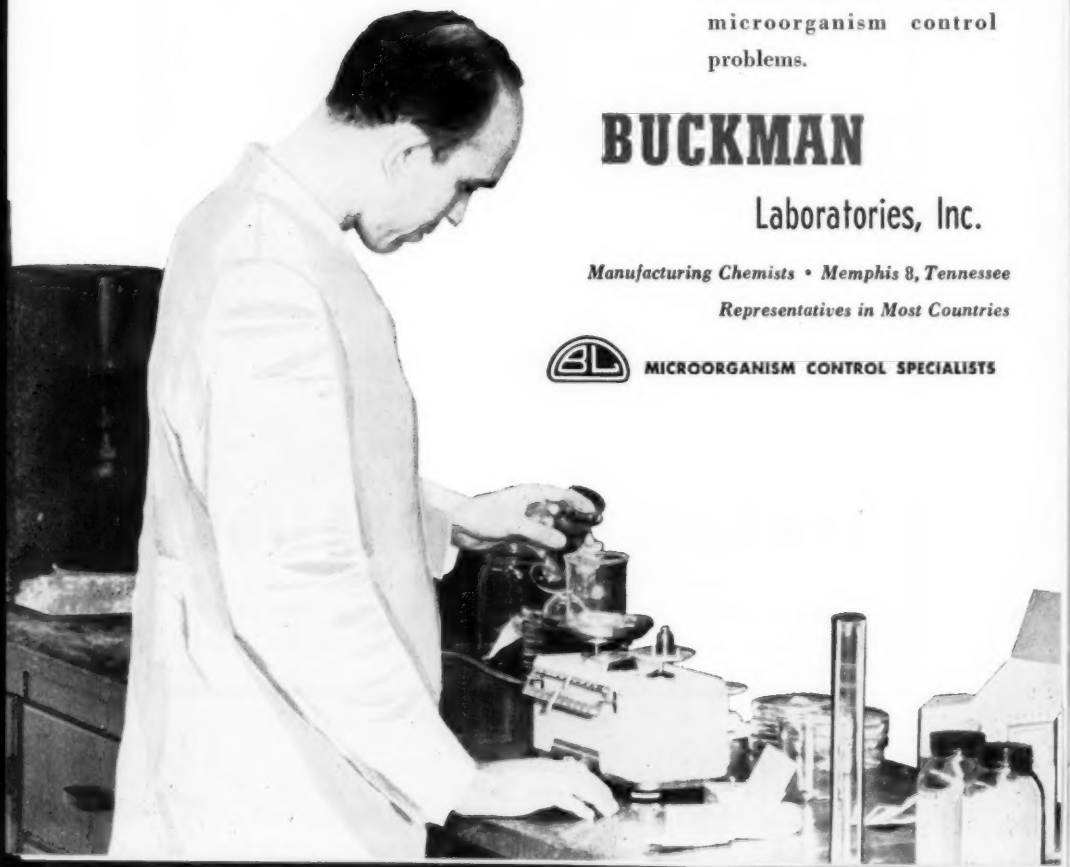

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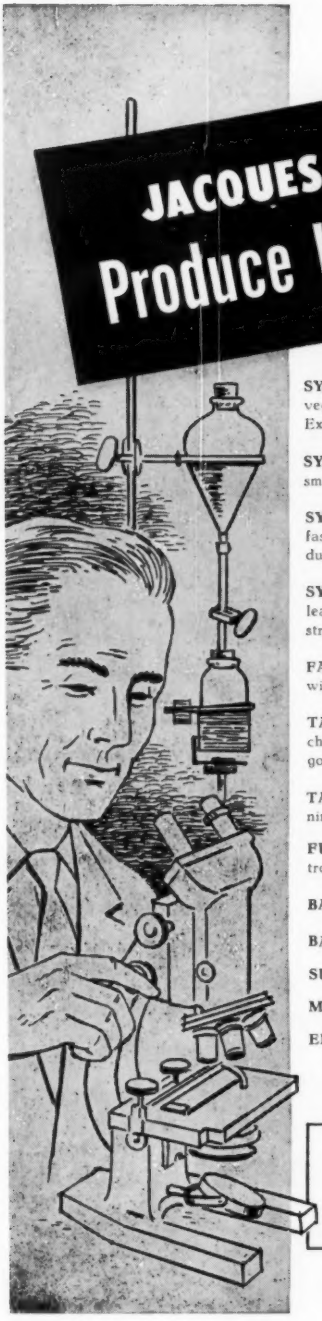

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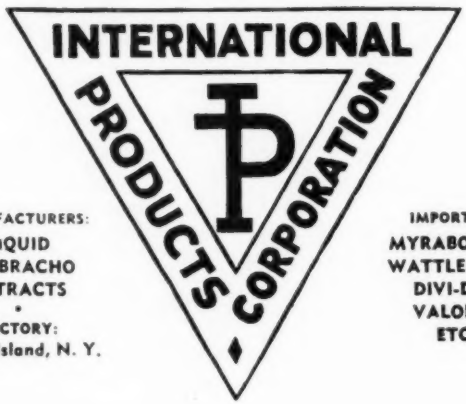

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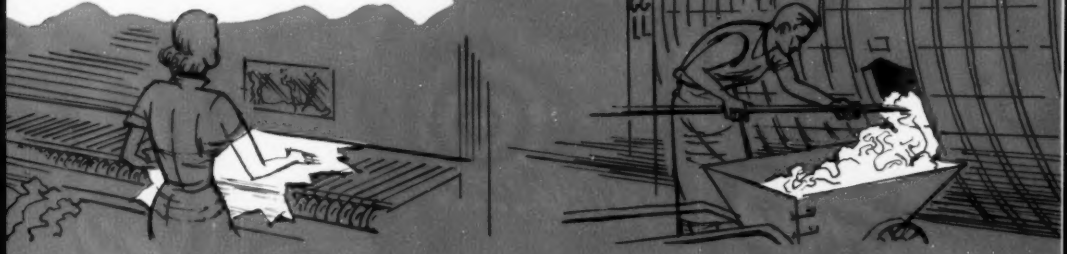

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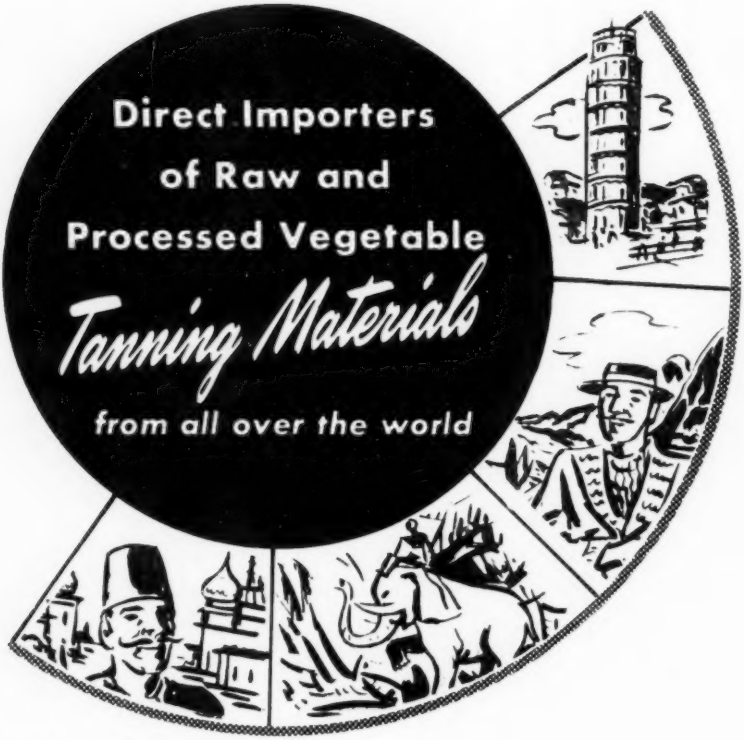

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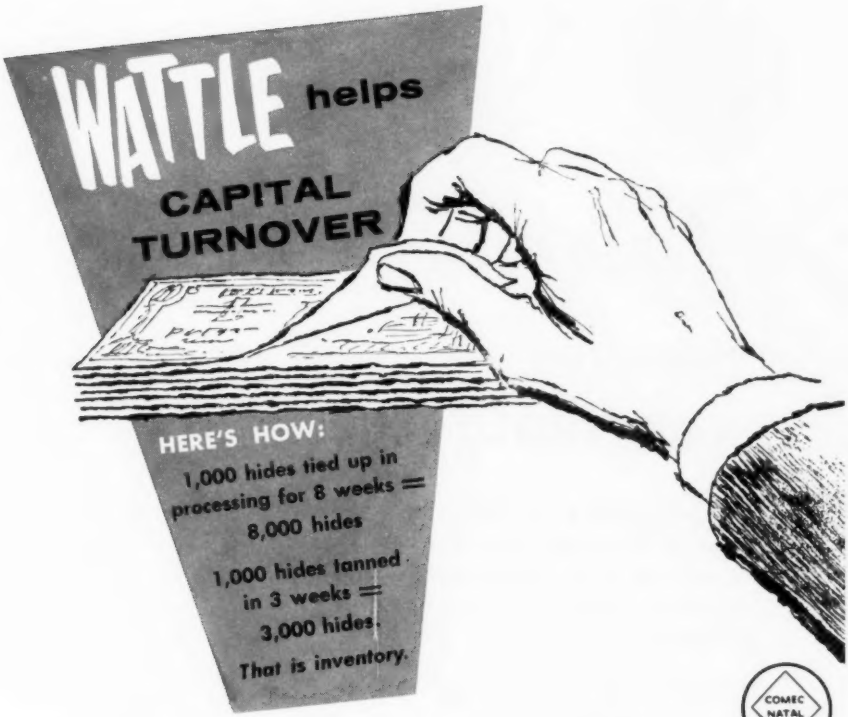
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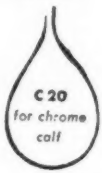

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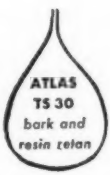

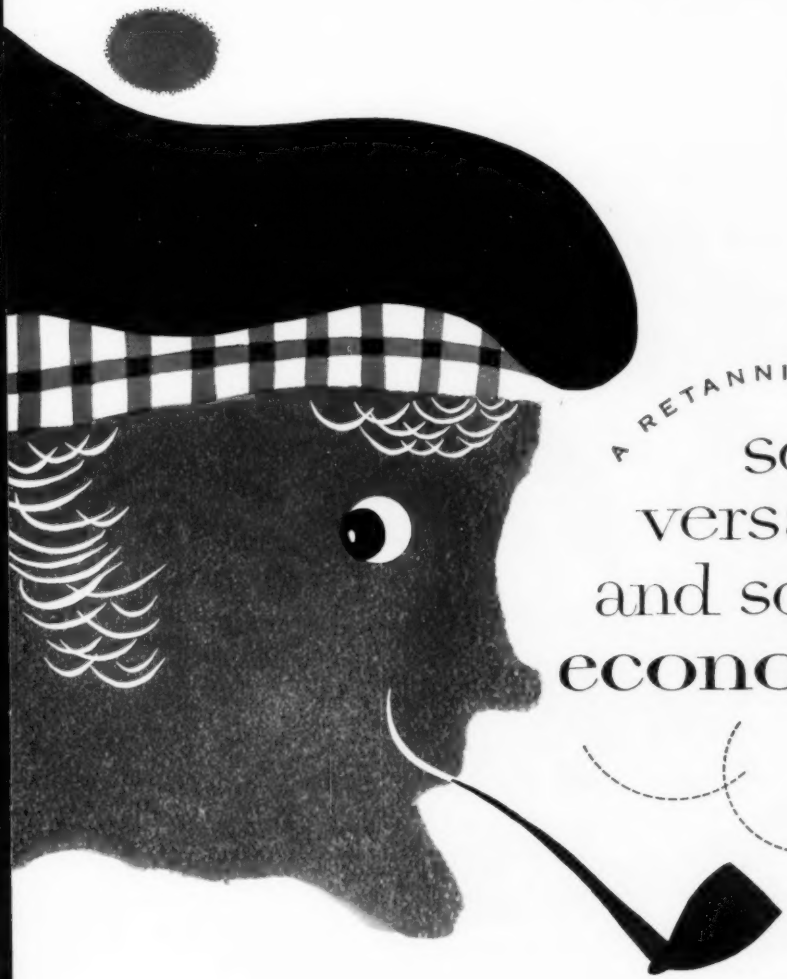

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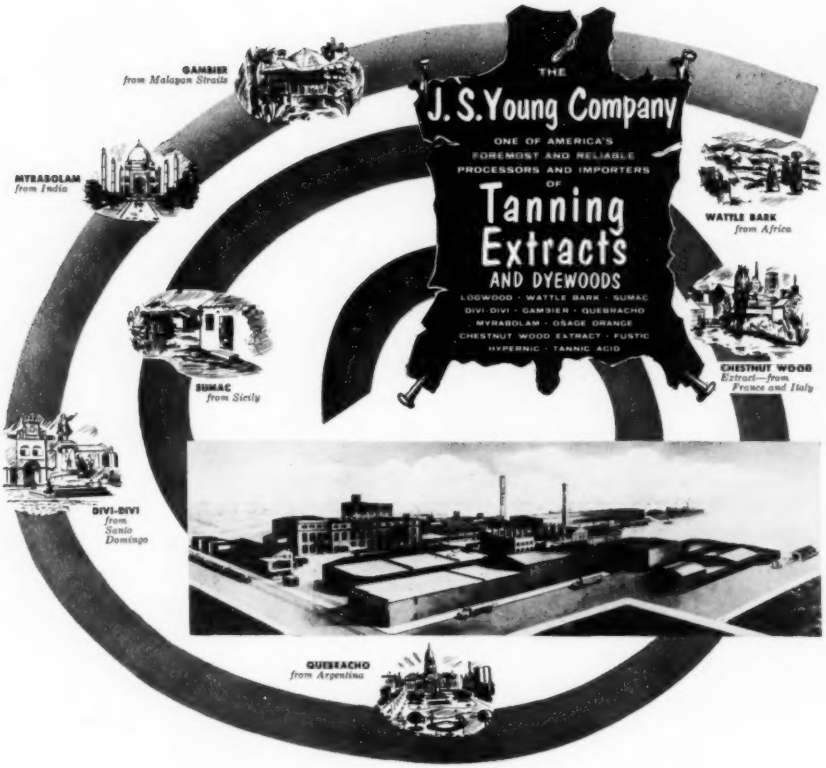

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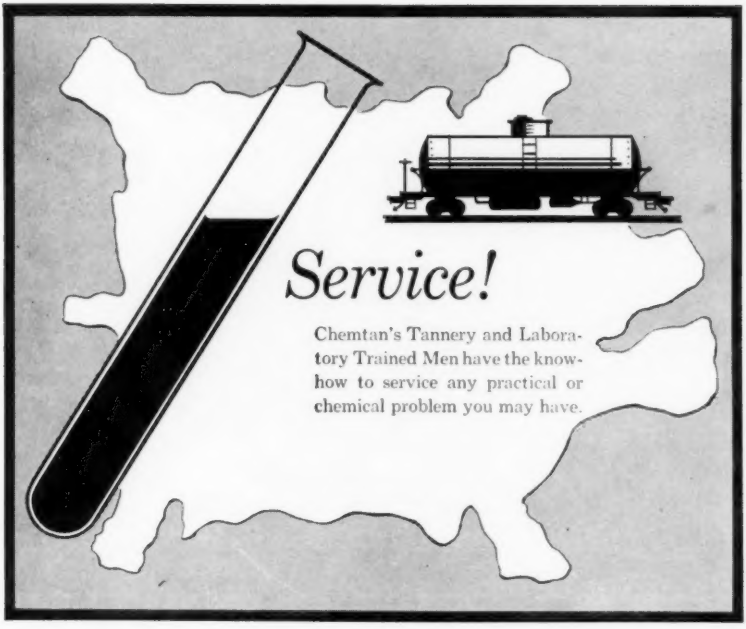
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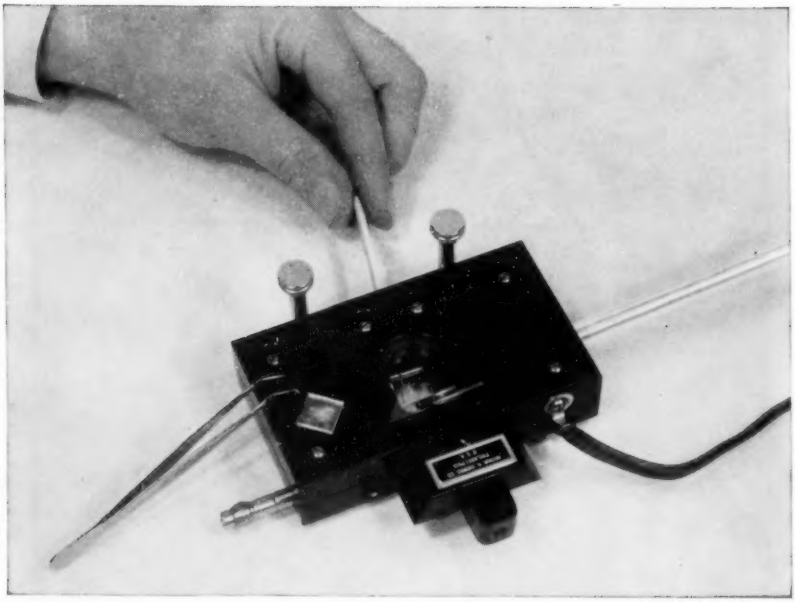

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6893-N. "Fusion Methods in Chemical Microscopy", by Walter C. McCrone *(Interscience Publishers, Inc., 1957),* 328-pp. Includes techniques for Thomas-McCrone Cold Stage **6.75**

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General correspondence concerning the Journal should be mailed to the Managing Editor.

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CANAIGRE INVESTIGATIONS

XII. DRYING CANAIGRE ROOTS IN A DIRECT-FIRED ROTARY DRIER

E. L. Griffin, Jr., V. A. Turkot, and N. F. Roger

*Eastern Regional Research Laboratory**
Philadelphia 18, Pennsylvania

ABSTRACT

Canaigre roots can be dried to a stable form in a rotary-type, direct-fired alfalfa drier. Root shreds dried to 12% moisture at an inlet air temperature of 900°F. showed no visible scorching or loss of tannin. The extractability of the tannin from the dried roots was substantially the same as from sun-dried shreds.

ABSTRACTO

Las raíces de canaigre pueden ser secadas a una forma estable en un secador de alfalfa rotativo y de fuego directo. Fragmentos de raíces secados a 12% de humedad por medio de una entrada de aire a una temperatura de 900 grados F. no mostraron chamusco ni perdida de tanino. La extracción del tanino de las raíces secas era substanciosamente la misma como de fragmentos secados al sol.

INTRODUCTION

Production of tanning extracts from canaigre roots (*Rumex hymenosepalus* Torr.) has been under study at this Laboratory in recent years (4). The canaigre roots used have been collected or grown by the Field Crops Branch of the Agricultural Research Service, USDA, at Mesa, Arizona. The roots must be harvested during the hot months while they are dormant. For storage throughout the year these roots have generally been shredded and sun-dried on concrete strips at the time of harvest. Most of our work was carried out on roots dried in this manner (5).

The sun-drying procedure was convenient for relatively small-scale test work, but is not too desirable for a production process. It requires large, hard-surfaced areas which will not shed pebbles or chips into the shredded roots. Even the concrete strips used for our tests were not ideal; quite a number of chips and stones from the concrete had to be removed before

*A laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

the dried shreds could be cut. This sun-drying procedure must be rapid to prevent loss of tannin by fermentation and root spoilage. It is, therefore, necessary to spread the shredded roots thinly in hot weather for the best results. Rain storms have damaged the roots and on one occasion a dust storm contaminated the shreds with excessive sand. For these reasons a more controllable mechanical drying process appears essential if dry storage is to be used.

Tray-drying or continous-belt-drying at air temperatures below 150°F. has been satisfactorily used, but these drying methods are relatively expensive. Hence drying tests were carried out in a small commercial-size multi-pass rotary drier of the type commonly used for alfalfa.

EQUIPMENT

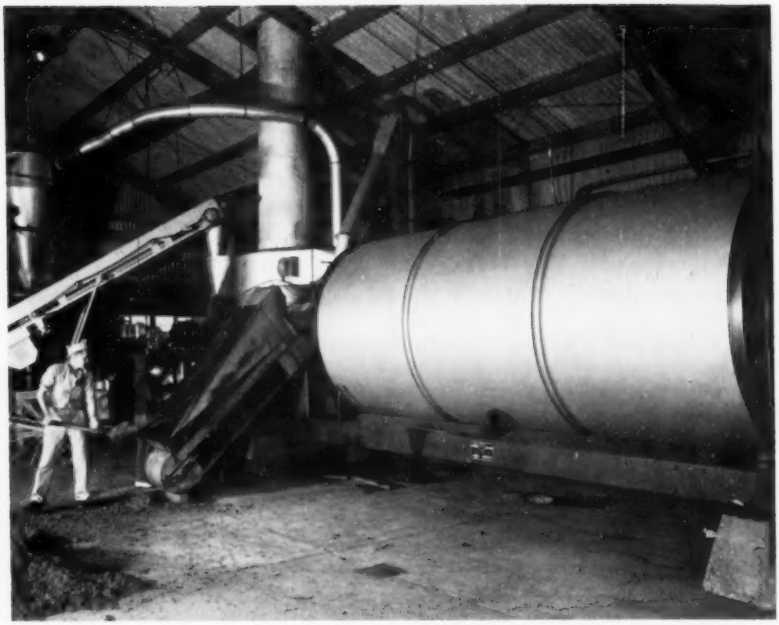
Washer.—A potato washer was used to clean the roots before shredding. It consists of a U-shaped trough divided into sections and equipped with rotating paddles that lift the roots from one compartment to the next while water flows continuously through the washer. Dirt and stones settle to the bottom of the trough and are flushed out periodically.

Cutter or Shredder.—The roots were cut either in a Fitzpatrick Model D comminuting machine* with sharp knives to pass through a screen with ½-inch diameter openings, or in a shredder equipped with three beet knives (H. Disston & Sons, Philadelphia, Pa., No. 9-40-A). The shredder was built at this Laboratory from a description by Kummer (2).

Drier.—The drier used was the Heil rotary dehydrator, Model PD 7-16, shown in Figures 1 and 2. This is a small commercial-size, double-pass, direct oil-fired, steel rotary drier commonly used for alfalfa. The rotating body, which is 16 feet long, is made up of three concentric cylinders, 2½, 5, and 7 feet in diameter, respectively. The inner cylinder is the combustion chamber. The oil burner is mounted at one end of this cylinder and protrudes from the main body, as shown at the right side of Figure 2. The drying air, drawn in by an exhaust fan through openings adjacent to the burner, is heated by mixing with the products of combustion.

The material to be dried is fed on to the elevator, from which a screw feeder forces it into the left end of the drier. Here it meets the heated air and products of combustion and is carried by them, in the annular space between the inner cylinder and the 5-foot cylinder, to the right end of the body, then back between the 5-foot cylinder and the outer one to the left end. Here the gases and the dried material enter the exhaust fan, which delivers them to the cyclone separator adjacent to the drier. The hot gases escape through the top of the separator, and the dried material falls through the bottom. Here a

*The mention of commercial products and companies anywhere in the paper does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.



Courtesy of U.S.D.A. Photo by M. C. Audsley

FIGURE 1.—Double-pass, direct oil-fired rotary drier.

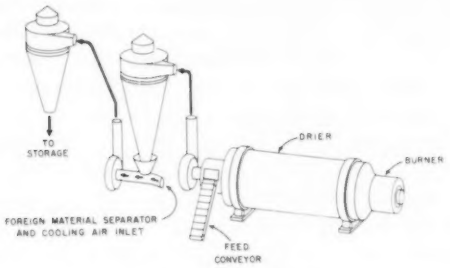


FIGURE 2.—Drier diagram.

stream of cold air entering a second fan picks up the dried material and sends it to a cooling cyclone separator. The velocity of this air is insufficient to pick up stones or gravel; any such material that has entered the drier falls out through a tee in the duct at this point. The dried material falls into bags at the bottom of the second cyclone.

TABLE I

DRYING CANAIGRE ROOTS* IN DIRECT OIL-FIRED ROTARY ALFALFA - TYPE DRIER

	SERIES I					SERIES II						
	Run 6	Run 4	Run 2	Run 5	Run 1	Run 10	Run 9	Run 7	Run 12	Run 11	Run 8	Run 13
Root cutter**	F	F	F	F	K	K	K	K	K	K	K	K
Cutter speed, r.p.m.	2300	2300	3180	2300	850	850	850	850	850	850	850	850
Inlet air temp., °F.	630	844	1005	1215	810	628	816	871	951	1045	1099	1240
Exit air temp., °F.	237	242	228	247	241	287	284	277	284	293	285	283
Feed rate, lb/hr	1156	2295	3200	4545	1896	908	1396	2079	1920	2400	2810	3360
Feed root moisture, %	63.3	61.0	60.1	62.2	61.2	71.3	69.8	71.0	70.3	69.2	70.5	73.0
Av. drying time, min.	——	——	——	——	——	12.1	10.4	13.0	12.0	12.5	7.2	15.3
Flue gas rate, cu. ft /hr (x1000)***	——	——	——	——	——	220	210	195	——	195	220	——
Product rate, lb /hr	511	1011	1440	1990	849	292	467	708	634	831	931	1024
Product moisture, %	17.1	11.4	11.3	13.7	13.2	11.9	11.4	13.8	10.0	11.1	11.5	12.9
Water evaporation, lb / hr	645	1284	1760	2555	1047	616	929	1371	1286	1589	1879	2336
Oil consumption, gal /hr	9	16	21.5	28.5	15	11.3	14.7	16.8	17.1	19.1	22.6	25.9
Water evaporation, lb /gal of oil	72	80	82	90	70	54.5	63.2	81.6	75.2	82.1	83.1	90.2
Thermal efficiency, %†	56.8	63.1	64.4	70.5	54.9	42.6	49.4	63.8	58.8	64.3	65.0	70.5
Drier capacity, lb. water evaporated/ hr /cu ft. ††	1.20	2.39	3.28	4.75	1.95	1.15	1.73	2.55	2.39	2.92	3.50	4.35
Tannin‡ %, m.f.b., feed roots	‡‡	‡‡	‡‡	‡‡	‡‡	28.8	29.4	29.0	28.8	28.1	29.5	30.1
" " " dried roots	30.7	31.5	31.2	29.3	31.7	28.9	28.9	29.3	27.4	26.9	25.8	23.4
Purity‡,%(soluble solids)feed roots	‡‡	‡‡	‡‡	‡‡	‡‡	49.1	48.9	50.0	50.4	48.3	49.7	51.3
" " " " dried roots	59.1	59.8	60.4	58.5	60.7	49.6	48.9	49.3	49.9	48.5	48.1	47.6
Iron, p.p.m., feed roots	150	140	——	140	119	——	——	——	——	——	——	——
" " dried roots	240	300	——	120	283	——	——	——	——	——	——	——

*Willcox strain roots grown 2 years from seed; Series I and II tests on roots harvested in successive years.
**F=Fitzpatrick comminuting machine; all roots cut with sharp knives to pass through ½" perforated screen.
K=Kummer shredder with 9-40-A beet knives.
***Standard conditions; dry, 60°F., 1 atmosphere.
†% of oil-heating value used to heat roots and evaporate water.
††Drying zone 537 cu. ft.
‡Determined by extraction with 50% acetone, evaporation of acetone (3), ALCA method (1) on residue.
‡‡Representative roots from Series I lot tray-dried at 125°F. contained 32.2% tannin, of 60.5% purity (soluble solids). This closely represents the feed analysis of all runs in Series I.

EXPERIMENTAL RESULTS

Two series of drying tests were made using two-year-old cultivated Willcox strain roots harvested in successive years. The drying data are summarized in Table I. Substantially identical roots were used in runs of a single series, except for run No. 13 where the roots used were from a slightly different blend. Since the strain of roots degenerated with successive seedings, the Series II roots had lower tannins and purities than those of Series I.

The Fitzpatrick cutter, which was used for all the Series I roots except one, produced chips considerably finer than ½ inch although a ½-inch screen was used. The Kummer shreds (run No. 1 of Series I and all of Series II) were as long as 1 to 2 inches with many smaller particles. They were materially coarser, on the average, than the roots cut by the Fitzpatrick machine.

A product moisture of about 12% was sought and, except for run No. 6, was obtained within reasonable limits for all runs. This was achieved by first controlling the inlet air temperature through adjustment of the fuel rate (since the fan speed was fixed), and then varying the rate of feeding the roots until the desired product moisture was approximately reached, as indicated by a Steinlite moisture tester.

For the Series II runs the average drying time of the roots in the drier was about 12 minutes. This was calculated from the dry weight of material left in the drier at the end of the run and the root solids feed rate. Flue gas rates were calculated for some runs from the oil feed rate and an Orsat carbon dioxide analysis of the flue gases. They averaged about 200,000 cu. ft. per hour (dry, 60°F., 1 atmosphere) with no apparent significant trend. These values are only rough approximations, however, since they were calculated from very low carbon dioxide values.

In both series of tests there was an increase in the tannin loss during drying as the inlet air temperature was increased, as shown in Table I and Figure 3. This increased loss was accompanied by visible scorching and darkening of the product roughly in proportion to the loss of tannin. The smaller particles, which dry first, were most scorched. When drying to 11 or 12% moisture, this damage became perceptible at inlet air temperatures above 900°F. Below this temperature the loss would be about 2% or less of the tannin fed.

Canaigre roots must be dried below about 18% moisture to prevent mold growth and loss of tannin during storage, but they should not be dried to a lower moisture content than is necessary. With excessive drying in this machine, which was observed during the early parts of some runs before equilibrium was reached, the product temperature rose above 212°F., causing visible scorching and substantial loss of tannin. One sample, dried to 6.3% moisture, lost 62% of its tannin, while another, dried to 8.0% moisture, lost 33% of its tannin. Drying to 11 or 12% moisture, as was done in the tests reported, kept tannin destruction to a minimum because the average product temperature did not rise above about 212°F.

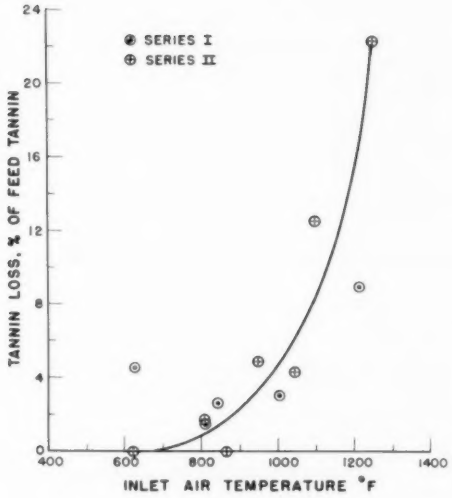


FIGURE 3.—Variation of tannin loss with inlet air temperature during rotary drying of canaigre roots.

The scorching obtained with overdrying, or drying at too high an inlet air temperature, was a function of the relative particle sizes as well as the inlet air temperature and the final product moisture. Individual particles scorched only when they were dried to such an extent that evaporative cooling was no longer sufficient to keep them near the wet bulb temperature. This occurs first with the smaller particles, which become dry midway through the drier where the air temperature is still high enough to destroy tannin. Hence a uniform feed particle size would permit use of a higher inlet air temperature (and a higher root feed rate) to yield the same final product moisture without scorching, because all particles would dry at the same rate and drying could be more easily controlled.

For both series of tests the drier capacity and the thermal efficiency increased with the inlet air temperature, as shown in Figures 4 and 5. In each case the Series I curve is higher than the Series II curve because of the finer cut obtained in the Fitzpatrick cutter. The values for the one lot of Series I that was cut in the Kummer shredder (Run 1) were also below the other Series I points for the same reason.

The iron content of the roots was approximately doubled, from about 140 to about 280 p.p.m., by processing in this steel equipment as shown by the Series I data (Table I). This is not believed a serious increase, however, since color skivers did not show iron discoloration, and since the iron contents (m.f.b.) of concentrated tanning extracts produced from these rotary-dried roots were much lower than the iron contents of the dried roots (m.f.b.). Table II lists iron contents of extracts produced from the Heil-dried roots

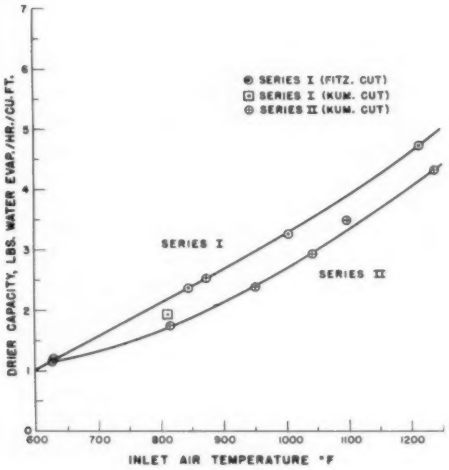


FIGURE 4.—Variation of drier evaporative capacity with inlet air temperature.

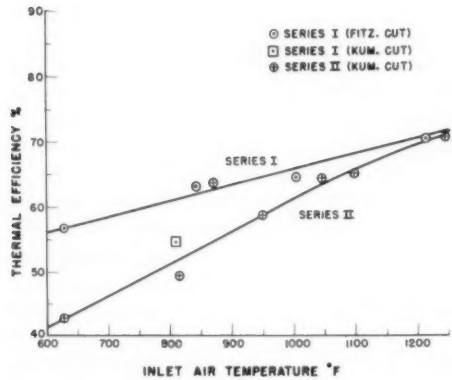


FIGURE 5.—Variation of thermal efficiency with drier air inlet temperature.

compared with the iron content of two extracts from roots not dried in contact with steel. The iron contents fluctuate too widely to show a significant difference.

Comparative extraction tests on the Series I roots dried at various temperatures in the rotary drier and on the same roots dried at 125°F. in a tray drier were made with water at 150°F. in a Kennedy-type continuous countercurrent extractor and in a single-batch mixing unit. Extractability of the tannin in the roots rotary-dried at all temperatures was about the same as that of the tannin in the roots tray-dried at low temperature which were taken as a standard. The only difference observed was that the rotary-dried roots became a little softer and more mushy during extraction.

TABLE II

IRON CONTENT OF CONCENTRATED CANAIGRE TANNING EXTRACTS

Root Drier	Root Drying Run	Extract No.	Inlet Air Temperature °F.	Iron p.p.m. m.f.b.
Tray	—	109	125	114
Tray	—	116	125	30
Rotary	6	114	630	120
Rotary	6	115	630	59
Rotary	4	112	844	28
Rotary	2	108	1004	66
Rotary	5	113	1215	110

CONCLUSIONS

Canaigre roots can be dried in a rotary, direct-fired, alfalfa-type drier without material loss of tannin where the conditions are such that little or no scorching is visible in the product. For maximum capacity and thermal efficiency the drier should be operated at the highest inlet air temperature which can be attained without excessive tannin loss. Such loss is minimized when the roots are dried only to the highest moisture content consistent with good storage.

In the Heil drier used for these studies the maximum desirable inlet air temperature is about 900°F. for roots being dried to about 12% moisture. A higher inlet air temperature could probably be used if the roots were dried to a higher moisture content or if the roots were cut to a more uniform particle size so that all particles would dry at the same rate.

ACKNOWLEDGMENT

The authors are indebted to A. Hoersch, Jr., for assistance in operating the drier; to F. P. Luvisi, M. E. Happich, and L. R. Ross for analyses; and to R. K. Eskew for general guidance in the work.

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A COLLABORATIVE STUDY ON THE CINCHONINE METHOD FOR DETERMINATION OF LIGNOSULFONATES IN VEGETABLE EXTRACT BLENDS*

by SVERRE DAHL, *Chairman*
with
Statistical Analyses by JOHN MANDEL, *Statistician*
National Bureau of Standards
Washington, D. C.

ABSTRACT

Collaborative analyses were made by six laboratories on 12 samples (one vegetable extract, four commercial lignosulfonate tanning agents, and seven blends of vegetable tanning materials and lignosulfonates). Analyses were done by the cinchonine method previously reported by this committee. The results were subjected to statistical analysis. The committee finds that the method is not sufficiently accurate to be adopted as a Provisional Method of ALCA.

ABSTRACTO

Análises en colaboración fueron hechos por seis laboratorios sobre doce muestras (un extracto vegetal, cuatro agentes comerciales de taninos lignosulfonados, y siete mezclas de materiales de taninos vegetales y lignosulfonados). Análises fueron hechos por el método de cinchonina previamente reportado por este comité. Los resultados fueron sujetos a un análisis estadístico. El comité juzga que el método no es lo suficientemente exacto como para ser adoptado como un Método Provisional de la ALCA.

INTRODUCTION

A previous report of this committee (1) deals with a survey of methods for the detection and estimation of lignosulfonates in vegetable extracts. The quantitative method that appeared to be most promising of those surveyed was based on the precipitation of lignosulfonates with cinchonine. It was in-

*Report of the Committee on Determination of Lignosulfonates, a Subcommittee of the Tannin Analysis Committee of ALCA. This subcommittee was composed of S. Dahl, *Chairman*, D. M. Balfour, R. E. Barnwell, Martin Baum, J. M. Hinkle, Virginia R. Power, and E. L. Rayfield. The Chairman of the Tannin Analysis Committee, when this work was done, was A. N. Kay.

vestigated by only two of the committee members and on only two types of lignosulfonate preparations. The main factors involved in the procedure were investigated. Even though the method appeared to be characterized by low accuracy and precision, it seemed doubtful if any further improvement in the procedure could be made.

The next task of the committee was to establish the capability of this method, as given in the previous report, to indicate the lignosulfonate content in typical commercial lignosulfonate preparations, alone and in the presence of typical vegetable extracts. For this purpose, a collaborative study was made, the results of which are reported here.

TABLE I

LIGNOSULFONATE MATERIALS USED IN THE COLLABORATIVE STUDY

	Bone-dry solids content, %†		MeO content, bone-dry basis, %		MeO content, "as is" basis, %		
Material*	Baum	Giguere	Baum	Giguere	Baum	Giguere	Average**
Maratan B (solid)	92.75	——	8.78, 8.80 Av. 8.79	8.92, 8.94 Av. 8.93	8.15	8.28‡	8.22
Lignosol TSD (solid)	90.71	——	7.49, 7.58 Av.7.53	7.68, 7.61 Av. 7.65	6.83	6.94‡	6.88
Totanin (solid)	91.06	——	8.10, 8.12 Av. 8.11	8.63, 8.64 Av. 8.64	7.38	7.87‡	7.63
Lactanx (liquid)	42.46	42.87	7.02, 7.04 Av. 7.03	7.09, 7.07, 7.07 Av. 7.08	2.98	3.04	3.01

*Maratan B—Sodium base lignosulfonate produced from basic calcium lignosulfonate as obtained on fractionating spent sulfite liquor from softwood pulping.
Lignosol TSD—Ammonia base lignosulfonate obtained from calcium lignosulfonate.
Totanin—Norwegian ammonia base lignosulfonate.
Lactanx—Magnesium-base lignosulfonic acid (pH 3.1). It contains acetic and lactic acids from fermentation of hemicellulose from spruce wood.
†Residue after drying to constant weight at 105°C.
‡Calculated from Mr. Baum's values for dry solids content.
**These values were used in subsequent calculations.

MATERIALS

Four typical commercial lignosulfonate preparations, together with data on their bone-dry solids contents and their methoxyl contents, are listed in Table I. These, together with a mixture of vegetable extracts, the composition of which is shown in Table II, were used in the study.

TEST PLAN

The test was designed so that statistical analyses of the results could be made. The objective was fourfold: (*a*) to determine the precision of the

TABLE II

VEGETABLE EXTRACT MIXTURE USED IN THE COLLABORATIVE STUDY

Extract	Solid Basis, %	Solution Basis, %
Myrobalans	10.0	3.33
Wattle	5.5	1.85
Valonia	12.0	4.00
Sulfited quebracho	25.0	8.33
Chestnut	22.5	7.50
Cutch	25.0	8.33
Water	—	66.66

cinchonine method within each participating laboratory; (*b*) to determine the agreement among laboratories; (*c*) to study the correlation of the results obtained by the cinchonine method with the concentration of lignosulfonate material as known from the preparation of the samples; and (*d*) to compare the results of the cinchonine method with those based on percent methoxyl as determined by the Zeisel method. This correlation is of interest since methoxyl content is also considered to be a measure of lignosulfonate content. However, because vegetable tannin materials also contain considerable methoxyl (1), the Zeisel method is unsuitable for determination of lignosulfonate in blends of unknown compositions.

The experimental design that was chosen required analyses of 12 samples. Four of these samples contained one of the respective lignosulfonates alone, one contained the mixture of vegetable tannins alone, and 7 samples were blends, each of which contained a known amount of one of the lignosulfonates in the vegetable tannin mixture. Duplicate portions of the 12 samples were bottled. Four of the resulting 24 bottles were sent to each of 6 laboratories, with no laboratory receiving duplicates. The laboratories analyzed each of the samples 4 times, once on each of 4 separate days, making a total of 16 determinations for each laboratory. Each sample was analyzed by 2 laboratories, each of which reported 4 results for each sample. The order in which the 4 samples were run each day was specified and altered from day to day in order to detect trends in within-day variations, if present.

The allocation of samples to laboratories formed a chain block design as shown in Table III. The theoretical basis for the analysis of variance of the data obtained by this design has been given elsewhere (2). Table IV, which contains all the experimental results, shows the detailed Latin-square design for each laboratory in terms of day and order in which each sample was analyzed.

The test samples were prepared by the committee's chairman. The samples were then analyzed as unknowns by the collaborating laboratories using

TABLE III

DISTRIBUTION OF SAMPLES TO COLLABORATING LABORATORIES

Collaborating Laboratory	Samples
1	A, C, F, I
2	J, H, B, D
3	L, G, K, E
4	I, J, C, B
5	D, L, H, K
6	E, A, G, F

TABLE IV

ANALYTICAL RESULTS, AS PERCENT CINCHONINE PRECIPITATE (C. P.) AND EXPERIMENTAL DESIGN

		Lab. 1		Lab. 2		Lab. 3		Lab. 4		Lab. 5		Lab. 6	
Day	Daily order	Sample	C. P.,%	Sample	C. P.,%	Sample	C.P.,%	Sample	C.P.,%	Sample	C.P.,%	Sample	C.P.,%
1	1	A	2.29	J	11.13	L	33.11	I	21.83	D	1.72	E	13.53
	2	C	27.42	H	11.68	G	4.68	J	9.66	L	29.13	A	2.45
	3	I	23.67	D	1.56	E	14.44	B	14.15	K	0.00	F	19.72
	4	F	20.59	B	16.77	K	0.00	C	25.05	H	12.11	G	4.99
2	1	C	27.44	H	11.11	G	4.67	J	9.81	L	29.17	A	2.38
	2	I	24.15	D	1.35	E	14.05	B	14.33	K	0.00	F	19.13
	3	F	23.07	B	14.55	K	0.00	C	24.98	H	11.48	G	4.78
	4	A	3.17	J	10.54	L	32.41	I	21.51	D	1.72	E	15.22
3	1	F	23.04	B	15.36	K	0.00	C	24.95	H	11.51	G	4.74
	2	A	2.69	J	11.06	L	32.93	I	21.83	D	1.44	E	16.21
	3	C	28.61	H	11.67	G	4.72	J	9.64	L	30.10	A	2.03
	4	I	25.60	D	1.58	E	13.92	B	13.50	K	0.00	F	19.88
4	1	I	26.05	D	1.75	E	14.54	B	14.26	K	0.00	F	20.30
	2	F	21.95	B	17.07	K	0.00	C	25.09	H	11.80	G	4.32
	3	A	2.41	J	10.59	L	32.26	I	21.82	D	1.75	E	14.38
	4	C	26.97	H	11.09	G	4.56	J	10.33	L	28.92	A	2.11

the method as given in the previous committee report (1) except for the following special instructions:

(*a*) Make a preliminary run on analytical solutions containing about 30 grams of the sample, as received, per liter of solution. From the results of the preliminary run, adjust the concentrations for successive runs so that for each sample the weight of the cinchonine precipitate is large enough to be accurately weighed, but not larger than about 0.5 gram. (The collaborators

were told that one sample, analyzed by 2 laboratories, would contain no lignosulfonate and would presumably not give any precipitate.)

(*b*) Report all results as percent cinchonine precipitate. (The method as given in the previous committee report specified the results to be reported as percent lignosulfonate, which was obtained by multiplication of percent cinchonine precipitate by the factor 1.35.)

The six committee members receiving samples for analysis were: D. N. Balfour, R. E. Barnwell, M. Baum, J. M. Hinkle, Virginia R. Power, and E. L. Rayfield. Mr. Balfour and Mr. Baum also received samples of the 4 lignosulfonate preparations for determination of their methoxyl contents by the Zeisel method. Mr. Balfour was ill at the time, and the samples sent to him were analyzed by his coworker, Mr. J. Giguere. Mr. Rayfield was unable to complete his analyses due to an injury. Mr. Dahl analyzed duplicates of the samples sent to Mr. Rayfield.

The methoxyl values were determined for each of the 4 lignosulfonate materials. From these values the methoxyl content of each blend was calculated in accordance with the amount of lignosulfonate material used in the preparation of the blend.

PREPARATION OF SAMPLES

Three of the commercial lignosulfonate materials used in this study and shown in Table I were solids in the form of air-dry powders, and one (Lactanx) was a liquid containing about 45% solids.

Solutions containing exactly 33.33% ("as is" basis) of the solids were prepared as samples of the 3 solid lignosulfonate materials. The Lactanx was used as submitted by the manufacturer. These 4 solutions constituted samples containing lignosulfonates and no vegetable tannins. Seven blends were prepared by mixing weighed quantities of one of these solutions with weighed amounts of a solution containing the vegetable extract mixture shown in Table II. The vegetable extract solution also was made up to contain exactly 33.33% total solids ("as is" basis) and constituted the sample containing *no* lignosulfonate. About 0.10% phenol was added as a preservative to each of the samples.

The 12 sample solutions prepared as described above were given identifying letters from A to H. Two portions of each sample were distributed to the respective laboratories according to the experimental design. The identities of the samples sent to each of the 6 collaborating laboratories are shown in Table III. The compositions of the 12 samples as derived from the preparations are included in Table VI.

RESULTS

Table IV shows the analytical results obtained and the experimental design used in the collaborative study. Table V is a summary of Table IV and

TABLE V

SUMMARY OF DATA GIVEN IN TABLE IV

Sample	Laboratory	Concentration of Analytical Solution* g./liter	Average % Cinchonine Precipitate†
C	1	30	27.61
	4	40	25.02
			Av. 26.31
F	1	30	22.16
	6	30	19.76
			Av. 20.96
I	1	30	24.87
	4	30	21.75
			Av. 23.31
L	3	15	32.68
	5	20	29.33
			Av. 31.00
K	3	70	0.00
	5	50	0.00
			Av. 0.00
B	2	—	15.94
	4	30	14.06
			Av. 15.00
A	1	30	2.64
	6	30	2.24
			Av. 2.44
E	3	30	14.24
	6	30	14.85
			Av. 14.54
D	2	—	1.56
	5	50	1.66
			Av. 1.61
H	2	—	11.39
	5	30	11.73
			Av. 11.56
G	3	70	4.66
	6	30	4.71
			Av. 4.68
J	2	—	10.83
	4	25	9.86
			Av. 10.34

*The figures given are grams of the sample solutions described in the section of this report entitled Preparation of Samples, diluted to 1 liter with water.

†From Table IV.

shows the average percent cinchonine precipitate found by each of the two laboratories analyzing a given sample as well as the average of the two laboratories. Table VI is a comparison of the sample compositions, as derived from their preparation, and the analytical results obtained in this study. The variations in the ratios of lignosulfonate material to percent cinchonine precipitate (C.P.) given in the last three columns of Table VI indicate the constancy (precision) with which the analytical results (C.P.) reflect the known amounts of lignosulfonate present in the samples. This relationship will be discussed more fully under the statistical analysis of results.

TABLE VI

COMPARISON BETWEEN SAMPLE COMPOSITIONS, AS DERIVED FROM PREPARATIONS, AND ANALYTICAL RESULTS

Sample	Type	Type and Amount of Lignosulfonate Material in Sample as Derived From Sample Preparation: Solution Basis, %*	Bone-Dry Basis, %†	MeO Basis, %†	Analytical Results as Cinchonine Precipitate, %‡	Lignosulfonate Material Found, Solution Basis, %**	Ratio of Lignosulfonate Material to Cinchonine Precipitate (C.P.): % Solution: % C.P.	% Bone-Dry: % C.P.	% MeO: % C.P.
C	Maratan B	100.00	30.91	2.74	26.31	100.00	3.80	1.17	0.104
B	Maratan B	50.92	15.74	1.40	15.00	57.0	3.39	1.05	0.093
A	Maratan B	14.74	4.56	0.40	2.44	9.3	6.04	1.87	0.164
						Av.	4.41	1.36	0.120
F	Lignosol TSD	100.00	30.23	2.29	20.96	100.0	4.77	1.44	0.109
E	Lignosol TSD	75.07	22.69	1.72	14.54	69.4	5.16	1.56	0.118
D	Lignosol TSD	9.74	2.94	0.22	1.61	7.7	6.05	1.83	0.137
						Av.	5.33	1.61	0.121
I	Totanin	100.00	30.35	2.54	23.31	100.0	4.29	1.30	0.109
H	Totanin	45.10	13.69	1.15	11.56	49.6	3.90	1.18	0.099
G	Totanin	23.33	7.08	0.59	4.68	20.1	4.99	1.51	0.126
						Av.	4.39	1.33	0.111
L	Lactanx	100.00	42.46	3.01	31.00	100.0	3.23	1.37	0.097
J	Lactanx	31.97	13.57	0.96	10.34	33.4	3.09	1.31	0.093
						Av.	2.66	1.34	0.095
K	——	0.00	0.00	0.00	0.00	0.0			
						Over-all Av.		1.41	0.114

*Solutions are those described in the section of this report on Preparation of Samples.
†Calculated from data in Table I.
‡From Table V.
**The % C.P. found in each of samples C, F, I, and L was taken as representing 100% of the respective lignosulfonate materials.

In addition to the 12 samples described under Test Plan, 5 laboratories also analyzed two additional samples, coded 5 and 6, containing Lactanx.

These samples were analyzed because the results originally returned indicated much poorer interlaboratory agreement on sample L (straight Lactanx) than on any of the other samples. Subsequently it was discovered that the apparent disagreement was due to a misunderstanding regarding calculations. The data on the two additional samples were not included in the results of the planned test but are summarized in Table VIA.

TABLE VIA

SUPPLEMENTARY RESULTS ON SAMPLES CONTAINING LACTANX

	Sample 5*			Sample 6*			
Laboratory	No. of Det.	Av. % C.P.**	Range†	No. of Det.	Av. % C.P.**	Range†	Ratio‡
1	5	26.83	0.98	3	20.07	1.04	74.8
2	4	27.88	1.19	4	21.48	0.37	77.0
3	4	33.57	2.73	4	22.13	1.28	65.9
4	4	27.51	0.72	4	18.25	0.75	66.3
5	4	28.11	0.86	4	20.90	2.09	74.4

*Sample 5 was straight Lactanx as received from the manufacturer, and sample 6 was composed of 66.59% Lactanx and 33.41% water.
†Highest minus lowest value.
‡The value for sample 6 as percentage of the value for sample 5. According to preparation of sample 6, the theoretical ratio should be 66.59.
**C.P.—Cinchonine precipitate.

STATISTICAL ANALYSIS OF RESULTS

The statistical analysis consisted of four parts. First, the results for each laboratory were analyzed individually in order to determine whether systematic variations from day to day were present and to evaluate the precision of the results. The second part of the analysis consisted of a comparison of results among laboratories. Upon completion of the determination of intra- and interlaboratory precision of the cinchonine method, the results obtained by this procedure were compared with the amount of lignosulfonate material present in each sample. Finally, the results of the cinchonine method were compared with those obtained by the methoxyl method.

Intralaboratory Analysis.—Table VII summarizes the analyses of variance made for the results of each laboratory. Neither daily variations nor systematic trends due to the order in which the analyses were made appear to be present in any of the laboratories. Therefore, the sums of squares were pooled for each laboratory, yielding estimates of their respective standard deviations. Considerable differences in reproducibility are seen to exist among laboratories. It was first ascertained whether these differences could be due to chance fluctuation, by means of Bartlett's test for homogeneity of variances. The test showed that the differences are too large to be due to random effects. Another explanation for the observed differences in repro-

TABLE VII

PRECISION OF RESULTS WITHIN LABORATORIES

Source of Variation	Degrees of Freedom	Mean Square, for Laboratories*					
		1	2	3	4	5	6
Days	3	1.529	0.611	0.056	0.104	0.039	0.221
Order of determinations	3	0.388	0.342	0.088	0.014	0.050	0.126
Remainder	6	0.691	0.345	0.024	0.080	0.152	1.325
Pooled	12	0.827	0.411	0.048	0.070	0.096	0.418
Standard deviation		0.91	0.64	0.22	0.26	0.31	0.65

*In terms of percent cinchonine precipitate.

ducibility among laboratories is the possibility that the variability among replicate measurements is proportional to the true magnitude of the quantity measured. Since the laboratories did not all analyze the same samples, it would then follow that the laboratories to which samples of higher lignosulfonate content were allocated would tend to obtain larger variability among replicates. In order to test this possibility, an analysis of variance similar to that of Table VII was run on the logarithm of the measurements. If the variability were proportional to the magnitude of the measurement, such an analysis on the logarithms would have yielded a more homogeneous set of standard deviations than the original analysis. The results showed, however, that this was not the case. It may be concluded that the observed differences in reproducibility among laboratories are due neither to chance fluctuations nor to an increase in analytical error with increasing lignosulfonate content. The bottom row in Table VII gives the standard deviation characterizing the reproducibility of replicate determinations, in terms of percent cinchonine precipitate, for each laboratory.

Intralaboratory Analysis.—An analysis of variance was made on the average values for each sample in each laboratory, neglecting the differences in precision for the various laboratories. The latter approximation impairs somewhat the validity of the analysis, but does not seriously affect the detection of appreciable differences in accuracy among laboratories. The results, summarized in Table VIII, show that some disagreement can be found among laboratories, as evidenced by the significant mean-square for "systematic laboratory effects." They also show that even after adjustment of the results for *systematic* differences among laboratories, there remains an over-all lack of agreement among results obtained for the same sample in different laboratories. This lack of agreement is larger than the largest one observed among replicates within any one laboratory. Table IX summarizes the results of the intra- and interlaboratory precision study.

TABLE VIII

COMPARISON OF CINCHONINE RESULTS FROM SIX LABORATORIES

Source of Variation	Degrees of Freedom	Mean Square*
Systematic laboratory effects	5	11.442
Remainder	7	2.841

*In terms of percent cinchonine precipitate, and converted to individual determinations to allow comparison with Table VII.

TABLE IX

SUMMARY OF PRECISION STUDY

Type of Comparison	Standard Deviation*
Among replicate analyses made in the same laboratory	Varies from 0.22 to 0.91 according to laboratory involved. Best central value = 0.56.
Among analyses made in different laboratories, one analysis per laboratory	
1. No correction made for systematic differences among laboratories	Between 1.35 and 1.55. Using 0.56 as "within laboratory" std. dev., the corresponding value = 1.42
2. Correction made for systematic differences among laboratories	Between 0.86 and 1.15. Using 0.56 as "within laboratory" std. dev., the corresponding value = 0.97

*In terms of percent cinchonine precipitate.

Comparison of Cinchonine Method with Percent Lignosulfonate Material.—In Figure 1 the values of percent cinchonine precipitate are plotted against the percent lignosulfonate material in solution. The former are adjusted averages for the two laboratories in which each particular sample was analyzed, to eliminate systematic differences among laboratories. A regression analysis of the results reveals that for all 4 preparations the straight line cinchonine precipitate and lignosulfonate material passes through the origin, indicating proportionality between these two quantities. However, the slope (factor or proportionality) is different for the different preparations, as shown by the least-squares fits in Figure 1 and in Table X. This is due mainly to the fact that the amount of solid lignosulfonate material varies for the different solutions so that 100% on the abscissa does not correspond to the same lignosulfonate content for all preparations. The agreement of the slopes relating the results of the cinchonine method to the "theoretical" concentrations of lignosulfonate material is much improved if these "theo-

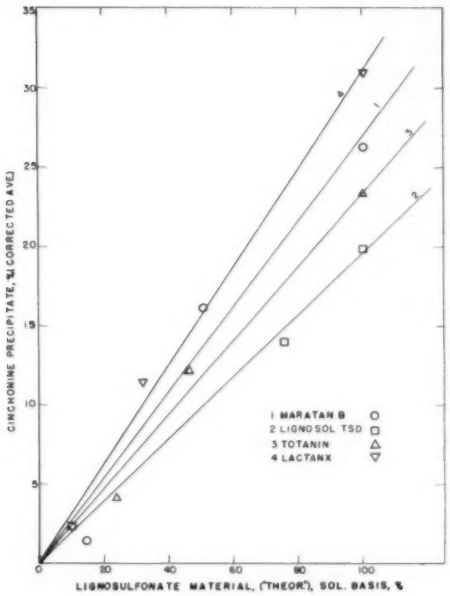

FIGURE 1.—Percentages of cinchonine precipitate found (corrected for systematic laboratory effects) versus percentages of lignosulfonate material in sample solutions as calculated from their preparation.

TABLE X

COMPARISON OF CINCHONINE METHOD WITH PERCENT LIGNOSULFONATE MATERIAL

Preparation	Ratio of % Cinchonine Precipitate To % Lignosulfonate Material	
	Solution Basis	Bone-Dry Basis
Maratan B	0.270	0.873
Lignosol TSD	0.194	0.642
Totanin	0.236	0.779
Lactanx	0.315	0.741

retical" values are expressed on a bone-dry basis, as can be seen in Table X and Figure 2. If the relatively small, though statistically significant, differences among these 4 slopes are disregarded, the best common value for the slope is 0.7520. Consequently, the ratio of dry lignosulfonate material to percent cinchonine precipitate is 1/0.7520 = 1.33, which is in good agreement

with the commonly accepted value of 1.35. (The 1.33 value for this ratio is more representative of the over-all data than the 1.41 average value found from the individual numerical ratios and given in Table VI.)

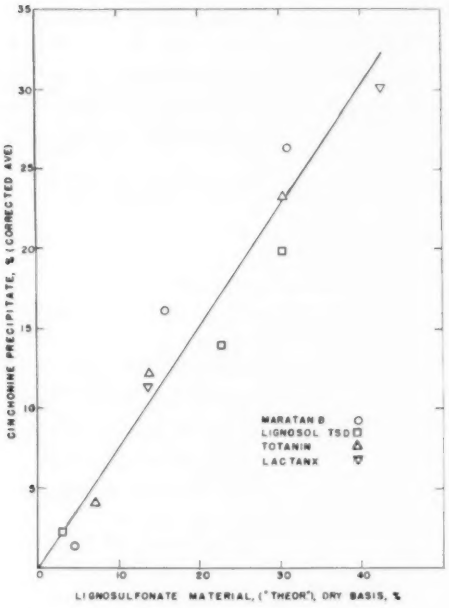

FIGURE 2.—Percentages of cinchonine precipitate found (corrected for systematic laboratory effects) versus percentages of "bone-dry" lignosulfonate material in sample solutions as calculated from their preparations and the moisture content of the four lignosulfonates.

The fit of the least-squares line in Figure 1 is somewhat poorer than would be inferred from the precision of the data, the latter being calculated from the interlaboratory agreement of results for any given sample. As inferred from the scatter of the points corresponding to a given preparation about the line corresponding to that preparation, the standard deviation is about 2.6 times the value it would have if the points fitted the line within experimental error. This large scatter may be due to either of the following two causes or to a combination of both. The first possibility is lack of linearity, in the sense that the amount of cinchonine precipitate is not strictly proportional to lignosulfonate content, over the entire range of lignosulfonate concentration in the samples. The second possible explanation is the presence of errors introduced in preparing the blends or the analytical solutions. The data are not sufficient to determine with confidence which of these causes of error predominates. There is no indication of curvature in Figure 1. In three instances, different blends from the same lignosulfonate material were analyzed by the same laboratory: samples A and C by laboratory 1, samples B and C

by laboratory 4, and samples E and F by laboratory 6. The ratios of cinchonine precipitate in these three cases were:

$$C/A = 10.46, \text{ with a theoretical value of } 6.78$$
$$C/B = 1.78, \text{ with a theoretical value of } 1.96$$
$$F/E = 1.33, \text{ with a theoretical value of } 1.33$$

The discrepancies between the observed and theoretical ratios in the first two cases are larger than can be accounted for by experimental error. Since both are obtained in the analysis of the Maratan preparation, and since they

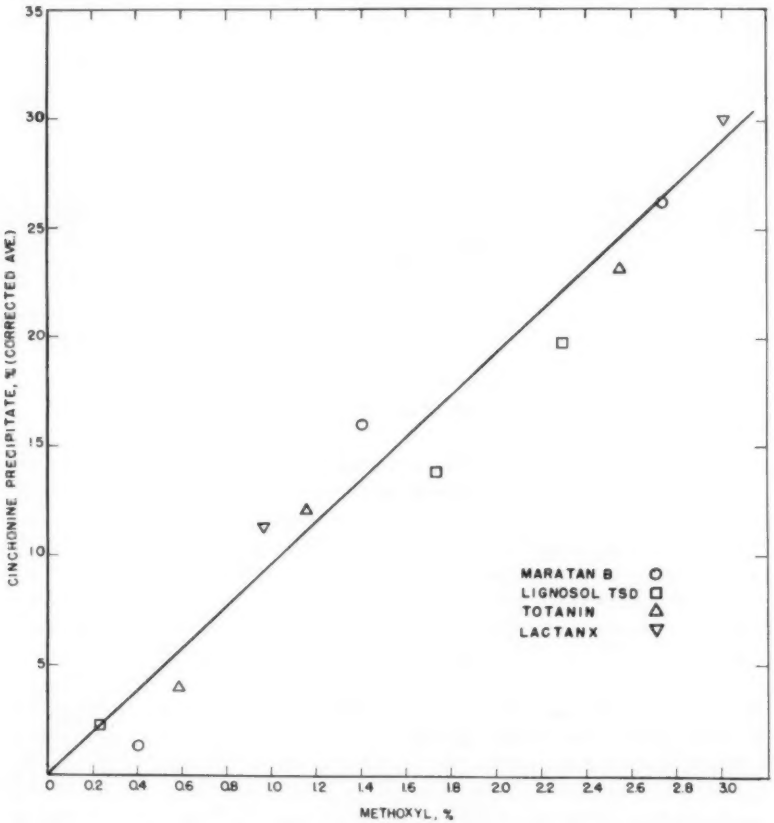

FIGURE 3.—Percentages of cinchonine precipitate found (corrected for systematic laboratory effects) versus percentages of methoxyl in sample solutions as calculated from their preparations and the methoxyl content of the lignosulfonates.

are in error in opposite directions, little can be inferred from these ratios, except perhaps that the scatter in Figure 1 is more likely to be due to dilution errors than to lack of proportionality between cinchonine precipitate and lignosulfonate concentration. However, such a conclusion is very tentative.

Comparison of Cinchonine and Methoxyl Results.——The results obtained by the two methods of analysis are plotted against each other in Figure 3. The agreement of the slopes for the various preparations is within experimental error. Consequently, a single line was fitted to all data. The value of the common slope is calculated to be 9.6. Thus, 1% of methoxyl (as determined by the Zeisel method) is equivalent to 9.6% of cinchonine precipitate, when both percentages are used as measures of lignosulfonates.

SUMMARY OF RESULTS

1. The intralaboratory standard deviations varied from 0.22 to 0.91% cinchonine precipitate, depending upon the laboratory involved. The reason for this variance is not known. Neither daily variations nor systematic trends due to the order in which the analyses were made appeared to be present in any of the laboratories.

2. There was a significant difference in accuracy among laboratories, i.e., some laboratories tended to have consistently high or low results for all samples they analyzed when compared to the average results from all laboratories. When this systematic difference was included in the interlaboratory precision, the standard deviation of the method was found to be between 1.35 and 1.55% cinchonine precipitate. If the systematic difference among the laboratories could be removed (that is, if the factors responsible for it could be identified and corrected), the precision of the method would be between 0.86 and 1.15% cinchonine precipitate. The values given here as measures of variability are standard deviations. It is common to consider a ± 2 standard deviation interval as a measure of precision. In the present case, such intervals may be used, but they will not include 95% of all measurements, because the standard deviations, as well as the average values, are based on a limited number of measurements. A statistical computation shows that the chances are of the order of 9 to 1 that the corresponding intervals will include at least 75% of all measurements (3). The over-all "absolute" error of a single determination may, therefore, be calculated to be ± 3.84% lignosulfonate (using a standard deviation of 1.42% cinchonine precipitate; 1.35 = factor for conversion of percent cinchonine precipitate to percent lignosulfonate; 1.42 x 2 x 1.35 = 3.84). The test results indicate that this "absolute" error is essentially the same whether the sample contains a high or a low percentage of lignosulfonate. The "percent relative error" therefore, will vary with the lignosulfonate content approximately as the following calculations show:

Lignosulfonate in Sample %	"Percent Relative Error"
5	76.8
10	38.4
20	19.3
30	12.8
40	9.6
50	7.7

It should be pointed out that the "percent relative error" for a single determination is reduced, for an average of several determinations, by the factor $\frac{1}{\sqrt{N}}$ where N stands for the number of determinations.

3. When the analytical results (percent cinchonine precipitate) were plotted against "theoretical" lignosulfonate percentages (as known from preparation of the sample solutions) it appeared, from a least-squares analysis, that for all 4 lignosulfonate materials used in this test the two percentages were proportional to each other. However, the fit of the lines was somewhat poorer than would be expected from the interlaboratory agreement of results. The reason for this is not clear but may be due to errors introduced in preparation of the samples or analytical solutions. When the "theoretical" percentages were expressed on bone-dry bases, there were comparatively small, though statistically significant, differences in the slopes of the four lines. The cinchonine method, therefore, gives reasonably concordant results for equal bone-dry weights of different lignosulfonate materials. The best common value for the slope gave 1.33 as the ratio of percent bone-dry lignosulfonate material to percent cinchonine precipitate, which is in good agreement with the commonly accepted value of 1.35 for this ratio.

4. Plots of percent cinchonine precipitate versus percent methoxyl showed, on the basis of a least-squares analysis, that for all 4 lignosulfonate materials these percentages are essentially proportional to each other. The agreement of the slopes for all four lines was within experimental error, and the value of the common slope was found to be 9.6. One percent methoxyl, therefore, is equivalent to 9.6% cinchonine precipitate when both percentages are used as measures of lignosulfonates.

CONCLUSIONS AND RECOMMENDATIONS

The cinchonine method is simple, fast, requires no special equipment, and appears to be generally applicable to lignosulfonates. It is not, however, very accurate or precise. This latter characteristic, in the opinion of the

majority of the committee members, makes it inadvisable to recommend the method for provisional adoption by the American Leather Chemists Association at the present time. The committee feels that it would not serve adequately for settlements of disputes of lignofulfonate contents of tannin materials. The committee also wants to state that all inferences drawn in this report pertain only to analyses of new blends and fresh liquors, such as those used in this study.

It is recommended that future ALCA committees continue the search for a better quantitative method. One that has recently been published (4) appears to warrant investigation, in addition to those mentioned in Mr. Jany's report (1). Studies on this problem now in progress in the paper industry, in which Mr. Baum of this committee is participating, may be fruitful in providing a method that can also be applicable to tannin materials.

The committee recommends that adoption of an ALCA official method be delayed until further progress is made in this field.

NOTE: In some collaborative analyses subsequent to the work herein reported, one collaborator obtained abnormally low results when using a tannic acid solution (reagent in the cinchonine method) that was several months old. From this, and the known susceptibility of such a solution to attack and probable deterioration by microorganisms, it is recommended that the method specify the use of a freshly prepared tannic acid solution as reagent.

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From the year 1283 the English leather industry gradually developed the organization of medieval guilds of "misteries" until, at the close of the fourteenth century, tanning in practically every town was controlled by these associations.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: The Rumpf Publishing Company, 1950.

STUDIES ON THE REACTIVE GROUPS OF COLLAGEN II. EFFECT OF THE REACTIVE GROUPS ON THE FIXATION OF CERTAIN ALDEHYDES

S. M. Bose and K. Thomas Joseph

Central Leather Research Institute
Madras, India

ABSTRACT

To obtain information as to the specific reactive groups of collagen that react with aldehydes, the fixation of formaldehyde, acrolein, and crotonaldehyde, by various modified collagens and by a polyamide, has been studied.

ABSTRACTO

Para obtener información acerca de los determinados grupos reactivos de colagenos que reaccionan con los aldehidos, la fijación de los formaldehidos, de la acroleína, y de los aldehidos crotonicos, por medio de varios colagenos modificados y por una poliamida, ha sido estudiada.

INTRODUCTION

It is well known that formaldehyde, acrolein, and crotonaldehyde are active tanning agents. The reactions of collagen and formaldehyde have been exhaustively studied by different workers (1–6). Factors influencing the fixation of acrolein and crotonaldehyde have been studied recently by the authors (7). Although it is generally agreed that someone or other of the reactive groups of collagen, e.g., free amino group, guanidino group, hydroxyl group, carboxyl group, amide group, or peptide linkage, may be involved in the fixation of tanning agents, it has not yet been definitely established which of the reactive groups actually take part in the reactions with these aldehydes. The effects of deamination (1,2,8,9), methylation (8,9), and partial destruction of the guanidino group (3) of collagen on the fixation of formaldehyde have been studied. The effect of acylation and deamidation of collagen on the fixation of formaldehyde has received no attention. No work has yet been done on the effect of modification of any of the reactive groups of collagen on the fixation of acrolein and crotonaldehyde. In the present investigation, systematic work has been carried out on the effects of benzoylation, acetylation, methylation, deamidation, de-

amination, and guanidino group destruction in collagen on the fixation of formaldehyde, acrolein, and crotonaldehyde at different pH values. In order to demonstrate the part, if any, taken by the peptide linkage in the aldehyde fixation, the reactions of these aldehydes with a polyamide Ultramid 6A, which is practically devoid of the ionic groups but contains peptide linkages similar to those of collagen, have also been studied. A comparative study of this nature may help to throw some light on the mechanism of collagen-aldehyde reactions.

EXPERIMENTAL

Preparation and Analysis of Modified Collagens.—Purified collagen was prepared from the butt of a fresh buffalo hide by the method of Highberger (10) as modified by Bose, Madhava Krishna, and Das (11). In a previous communication (12), details of the preparation of a few modified collagens and the extent to which the different groups were affected by modification were discussed by the authors. The same methods have been followed in the present investigation. The following modified collagens were prepared:

a. The free amino and guanidino groups of collagen were benzoylated by treatment with benzoyl chloride in anhydrous pyridine and carbon disulfide.

b. The quantitative acetylation of the amino and hydroxyl groups of collagen was effected by treatment with acetic anhydride in presence of formic acid and ethyl acetate.

c. About 50% of the hydroxyl groups of collagen were acetylated selectively by means of acetic anhydride in presence of thiocyanic acid.

d. All the free amino groups of collagen were selectively acetylated with acetyl pyridinium chloride.

e. About 70% of the arginine in collagen was destroyed by treatment with sodium hypobromite.

f. The carboxyl groups of collagen were specifically methylated with methyl alcohol in presence of hydrochloric acid by the method of Fraenkel-Conrat and Olcott (13) as adopted by Burton, Danby, and Sykes (14).

g. Collagen was deaminated with nitrous acid by the modified method of Bowes and Kenten (9).

Sixty-one percent of the amide groups of collagen were destroyed by treatment for 14 days with saturated lime water. The limed stock was first washed with dilute acetic acid and sodium chloride solution, then with distilled water, and finally was dried over P_2O_5 under vacuum.

The total benzoyl substitution in benzoylated collagen was determined (12) from the difference in total nitrogen content of collagen before and after benzoylation. The total acetyl groups in acetylated collagen were estimated (12) by the modified transesterification method of Whistler and Jeanes (15). The N-acetyl groups were estimated by the method described by Green, Ang, and Lam (16). The O-acetyl values were obtained as the difference between total and N-acetyl. Arginine was estimated by the modified method of Macpherson (17). The total methoyxl groups in methylated collagen were estimated by the method of Belcher, Fildes, and Nutten (18). The free amino nitrogen was determined by the modified method of Doherty and Ogg (19). The amide nitrogen was estimated by the method of Burton, Danby, and Sykes (14).

Preparation of Polyamide.—Ultramid 6A was made more reactive by the method of Gustavson and Britta Holm (20). After the powdered material was dissolved in boiling methanol, it was precipitated by stirring the solution into cold water. The precipitate was washed thoroughly and dried in vacuum over P_2O_5. The dried material was analyzed (19) for free amino nitrogen.

The results of all the analyses are presented in Table I.

Treatment with Aldehydes.—2.0 g. portions of dry collagen were weighed into glass-stoppered conical flasks and mixed with 100 ml. of 1.5% formaldehyde, acrolein, or crotonaldehyde solutions, the pH values of which were previously adjusted to different values and suitably buffered by mixtures of citric acid and sodium phosphate solutions. The flasks were allowed to stand at 33°C. for 48 hours. The tanned collagen samples were thoroughly washed until shown to be free from any free aldehyde by testing with Schiff's reagent. The amount of formaldehyde fixed by collagen was determined by the previously standardized colorimetric method (21) using chromotropic acid as the color reagent. The amounts of acrolein and crotonaldehyde fixed by collagen were estimated by the standard colorimetric method (7) using m-phenylenediamine hydrochloride as a color reagent. The moisture content of a portion of the washed sample of collagen was determined in each case by drying to constant weight at 100°C. under vacuum, and the number of millimoles of the aldehyde fixed by 1.0 g. of dry collagen was calculated. The free amino groups of unmodified collagen, before and after aldehyde fixation, were also estimated (19).

The fixation of the aldehydes by Ultramid 6A was studied in an identical manner except that the amount of the aldehyde fixed was determined (7,21) by the indirect method of estimating the aldehyde left in the residual liquor and the total washings.

The results are presented in Table I.

TABLE I

ANALYSIS OF MODIFIED COLLAGENS AND FIXATION OF FORMALDEHYDE, ACROLEIN, AND CROTONALDEHYDE, BY MODIFIED COLLAGENS AT DIFFERENT pH VALUES

Substrate Used	Extent of Modification	Amide N	Free Amino Group	Formaldehyde Fixed*			Acrolein Fixed*			Crotonaldehyde Fixed*		
				pH 5.1	pH 7.0	pH 10.1	pH 5.1	pH 7.0	pH 10.1	pH 5.1	pH 7.0	pH 10.1
Untreated collagen	None	0.31	0.37	0.20 †(0.27)	0.44 (0.15)	0.78 (0.11)	0.25 (0.24)	0.30 (0.22)	0.40 (0.20)	0.21 (0.25)	0.22 (0.23)	0.34 (0.21)
Deaminated collagen	all ε-amino groups destroyed	——	0	0.10	0.22	0.63	0.12	0.17	0.35	0.10	0.12	0.29
Lime-treated collagen	61% amide groups destroyed	0.12	0.37	0.14	0.32	0.74	0.19	0.21	0.38	0.15	0.16	0.32
Hypobromite-treated collagen	70% guanidino groups destroyed	——	0.65	0.20	0.43	0.62	0.25	0.29	0.35	0.21	0.21	0.29
Methylated collagen	0.82 m.moles methoxyl introduced /g.	——	0.30	0.19	0.43	——	0.24	0.29	——	0.20	0.21	——
Acetylated collagen (A)	2.1 m.moles. acetyl/g.	——	0	0.10	0.15	——	0.12	0.13	——	0.10	0.10	——
Acetylated collagen (B)	0.80 m.moles. acetyl/g.	——	0.35	0.19	0.40	——	0.24	0.27	——	0.20	0.20	——
Acetylated collagen (C)	0.56 m.moles. acetyl/g.	——	0	0.11	0.21	——	0.12	0.18	——	0.10	0.13	——
Benzoylated collagen	0.7 m.moles benzoyl/g.	——	0	0.10	0.21	——	0.12	0.16	——	0.10	0.12	——
Ultramid 6A	——	——	0.05	0.02	0.04	0.04	0.02	0.03	0.03	0.02	0.03	0.03

*Expressed as millimoles per gram of dry collagen.

†The data given in parentheses are for free amino groups of collagen after aldehyde fixation. Dr. Highberger (private communication) is of the opinion that the presence of free amino groups after formaldehyde tannage may be partly due to their liberation during the actual determination, by reversal of the formaldehyde combination by the acid used in the deamination.

DISCUSSION

The data on the fixation of formaldehyde, acrolein, and crotonaldehyde by untreated collagen under different pH conditions confirm previous findings that the amount of the aldehyde fixed in the acid region is smaller than that fixed at the neutral pH, while that fixed at the alkaline pH is the highest. Highberger and Retzsch (2) reported that very small amounts of formaldehyde were fixed by collagen in the acid region, and that with increasing pH the fixation gradually increased, remained constant between pH 7 and 8, and then increased again as the pH was further increased. Similar results were obtained by the authors (7) in the case of the fixation of acrolein and crotonaldehyde by collagen. Such results were explained by Highberger and Retzsch and by Bowes and Kenten (8) by suggesting that at pH values lower than 7, only the free amino groups of collagen take part in the reaction; the constant fixation between pH 7 and 8 presumably marks the completion of the reaction of the aldehyde with the free amino groups; at more alkaline reactions the guanidino groups take part in the reaction and fix additional amounts of the aldehyde.

However, the data for the free amino groups of unmodified collagen, before and after aldehyde fixation at different pH values, indicate that irrespective of the pH of the reaction medium, the three aldehydes do not react quantitatively with the available amino groups under the conditions of tanning employed. Theis and Ottens (5) also reported that formaldehyde did not react with all the available amino groups of collagen even under highly alkaline condition. The data obtained on the fixation of formaldehyde, acrolein, and crotonaldehyde by modified collagens suggest that the amount of the aldehyde fixed in excess of the free amino groups involved is due to reaction with several other groups of collagen.

Removal of the ε-amino groups of collagen by deamination greatly reduces the fixation of all three aldehydes at the acid and neutral pH, but at the alkaline pH the reduction in the fixation is comparatively small. On the other hand, there is practically no reduction in the fixation of the aldehydes at the acid and neutral pH values after the destruction of about 70% of the guanidino groups in collagen, but at the alkaline pH some reduction in fixation has been observed. As discussed in a previous communication (12), the increase in the free amino groups in the hypobromite-treated collagen is due to the replacement of at least some of the guanidino groups by amino groups. These results therefore lend further support to the suggestions of Highberger and Retzsch (2) and of Bowes and Kenten (8), and indicate that some of the free amino groups of collagen take part in the reaction with the aldehydes in the acid and neutral region and that the additional fixation of the aldehydes from alkaline solution may be partly due to the reaction of some of the guanidino groups with the aldehydes.

Apart from the 1.75 millimoles per gram of free hydroxyl groups which are present in collagen, deamination replaces the amino groups by hydroxyl groups. Since the acetals which are formed by the reaction of the aldehyde with the hydroxyl group are unstable in acid, the hydroxyl groups may not take part in the reaction at the more acid pH, but the possibility of such a reaction in neutral and alkaline pH cannot be entirely ruled out. That the hydroxyl groups may take part in the fixation of the aldehydes is also indicated by the results obtained on the fixation of the aldehydes by acetylated, benzoylated, and deaminated collagens. In a previous communication (12), it was reported that under the conditions of benzoylation, no hydroxyl groups of collagen took part, and that the benzoyl groups introduced (0.7 millimoles per gram) were predominantly attached to the free amino and guanidino groups of collagen. In acetylated collagen A, containing 0.39 millimoles N-acetyl and 1.71 millimoles O-acetyl per gram of collagen, all the amino and hydroxyl groups of the collagen were acetylated. In acetylated collagen B, containing 0.02 millimoles N-acetyl and 0.78 millimoles O-acetyl, about 50% of the hydroxyl groups were selectively acetylated. In acetylated collagen C, wherein 0.39 millimoles N-acetyl and 0.17 millimoles O-acetyl were introduced, all the free amino groups, and only a small fraction of the hydroxyl groups, were acetylated. The increase in the fixation of the aldehydes by acetylated collagen C, benzoylated collagen, or deaminated collagen as compared to that by acetylated collagen A at the neutral pH, may be due to the reaction of the hydroxyl groups with the aldehydes.

A slight reduction in the fixation of the aldehydes by lime-treated collagen has been observed at acid and neutral pH; at the alkaline pH the reduction is still smaller. As 61% of the amide groups are destroyed in the lime-treated collagen, it appears that the amide groups may take part in the fixation of the aldehydes at the acid and neutral pH. The fixation of the aldehydes by deaminated and other modified collagens at acid and neutral pH may therefore be at least partly due to the reaction of the amide groups with the aldehydes.

As almost the same amounts of the aldehydes are fixed by methylated and untreated collagen, it appears that the carboxyl groups do not take part in the fixation of the aldehydes. Bowes and Kenten (8) found that the fixation of formaldehyde by methylated collagen was greater than that by untreated collagen at all pH values. As the methoxyl groups are hydrolyzed at alkaline pH values, the increased fixation observed by Bowes and Kenten (8) was not caused by the methylation of the carboxyl groups. Bowes and Kenten (8,9) however, prepared methylated collagen by the action of dimethyl sulfate which produced considerable degradation of the collagen molecule. The use of dimethyl sulfate–treated collagen for comparative tanning experiments has been criticized by Kremen and Lollar (22).

It has also been observed that only negligible amounts of the aldehydes are fixed by Ultramid 6A. This slight fixation may possibly be due to the amino end groups of the polyamide, and not to the keto-imide linkage. It may, therefore, be assumed that there is no primary reaction between the aldehydes and the peptide groups, but, as Bowes and Kenten (8) suggested, there may be a possibility of secondary condensation of the peptide groups with aldehyde molecules already fixed by other groups.

Gustavson (6,23) and Fraenkel-Conrat and Olcott (24) have suggested that simple blocking of the reactive groups of proteins by tanning agents is insufficient to explain the increased structural stability resulting from tanning, and that new interchain linkages are formed, in which the tanning agent is combined with more than one polypeptide chain. Thus two groups belonging to different polypeptide chains may be linked by the aldehydes, forming methylene bridges. Nitschmann *et al.* (25,26) studied the reactions of casein with formaldehyde and found evidence of the formation of such methylene bridges. Fraenkel-Conrat and his associates (27–30) studied the reactions of formaldehyde with gramicidin and other proteins and discussed in great detail the cross-linking of the reactive groups of the protein by formaldehyde. As the amino-acid composition of collagen is different from that of casein, gramicidin, and other proteins, and as the collagen used was found (31) to contain no tryptophane and very little tyrosine and histidine, the results obtained in the present investigation with collagen may not be strictly comparable with those obtained by Nitschmann *et al.* and Fraenkel-Conrat *et al.* Moreover, it is still a matter of great speculation which group or groups of proteins of different composition are actually available for the bridging reactions and cross-linking with aldehydes of different constitution.

SUMMARY

The fixation of formaldehyde, acrolein, and crotonaldehyde by untreated collagen and several modified collagens (deaminated, deamidated, methylated, hypobromite-treated, acetylated, and benzoylated) and also by Ultramid 6A has been studied in acid, neutral, and alkaline pH.

It has been observed that at acid and neutral pH the free amino and amide groups, at alkaline pH the guanidino groups, and at the neutral and alkaline pH the hydroxyl groups take part in the reactions with the aldehydes. It has also been shown that there is no primary reaction between the aldehydes and the peptide groups or the carboxyl groups.

ACKNOWLEDGMENT

Our thanks are due to the Director, Central Leather Research Institute, for his keen interest in the work and to Badische Anilin & Soda Fabrik, Ludwigshafen, Germany, for kindly supplying Ultramid 6A as a gift sample.

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Received December 13, 1956.

Steam power was first applied to leather production in Woburn, Mass. in 1835. Power utilization not only increased plant and labor productivity in tanning but gave an important impetus to tannery mechanization. One of the greatest contributions to modern tanning technique was the perfecting by Mellen Bray in 1840 of the fleshing and unhairing machine . . . The fleshing and unhairing machine not only brought about a great increase in labor productivity, but paved the way for the conversion of the tanning industry from a handicraft to mass production.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: The Rumpf Publishing Company, 1950.

LIFE LINES

Brief Biographies of Our Contributors

S. M. Bose.—See the January, 1957, issue of *JALCA*.

Sverre Dahl received his B. S. degree from Drury College, Springfield, Mo., and did graduate work at the University of Kansas City, Kansas City, Mo. Prior to joining the National Bureau of Standards in 1947, he worked for the Bureau of Reclamation at Fort Collins, Colorado, and in private industry in the midwestern states. Since coming to N.B.S. he has been active in the development of test methods for leather and has served on several ALCA committees. In addition, he has been engaged in studies on mildew-proofing treatments for leather. He joined ALCA in 1951.

Edward L. Griffin, Jr., is Supervisor of the Processing Development Unit of the Engineering and Development Section at the Eastern Utilization Research Branch, U.S.D.A. He was formerly Supervisor of the Tanning Products Development Unit at the same laboratory where he has carried out pilot-plant studies toward the utilization of a variety of farm crops since 1942. Before that he worked for James Lees & Sons. He holds degrees in chemistry and chemical engineering from Cornell University.

K. Thomas Joseph was born in Kerala, India. He graduated from the University of Madras in chemistry in 1951 and pursued his further studies in the University of Rajputana where he took his M. Sc. degree in organic chemistry, securing a high first class. He joined the biochemistry laboratory of the Central Leather Research Institute, Madras, in January, 1955, and since then has been working on the chemistry of skin and hide proteins. He has already published a few papers on this subject with special reference to collagen-aldehyde reactions and the reactive groups of collagen.

Norman F. Roger has a B. S. in Chemical Engineering from the University of New Hampshire, and an M. S. from the University of Pennsylvania. He also attended the University of Delaware Extension School. He served three years in the U. S. Army as a Combat Intelligence Officer and as a Petroleum Supply Officer in the U. S. Army Air Force. At the Eastern Utilization Research Branch of the U.S.D.A. he is a Project Leader and has worked on the development of domestic tanning materials. He is the author of papers

on the utilization of hemlock slabs as a source of tannins and the coauthor of others on the development of canaigre tannin extract manufacture.

VICTOR A. TURKOT received his B. S. in Chemical Engineering at the University of Pennsylvania in 1945; since then he has been employed as a chemical engineer at the Eastern Utilization Research Branch, U.S.D.A. He was formerly engaged in developing a commercial method of producing tannin from canaigre roots. At present he is developing methods of preparing dried fruit juices.

The Americans consume more animal production than any people in proportion to their numbers, being near to the greatest foreign sources of unmanufactured hides, and being invited to sheep, swine, and cattle farming by a redundancy of soil, with cheaper water and land, proper oils, lime and bark for leather making business than any other country. The leathern branch must continue to be very considerable and rapidly to extend and improve. It is not doubted that it is at present equal in value to the same branch in any other country in proportion to the population if the same qualities of goods be estimated at the same prices. These facts in relation to the leathern branch are of peculiar importance, as it is generally a manufacture by *hand* and not by machinery. They unanswerably prove our capacity even in the handicraft branches, and render our capacity for machine operations free from doubt or question.

—*Statement of Facts and Manufactures of the United States of America for the Year 1810.* Digested and prepared by Tench Coxe, Esq. of Philadelphia. A. Cornman, 1814.

In 1812 the duties on leather of 7½ per cent ad valorem, established in 1789, were increased in some cases to 35 per cent. Following the War of 1812 leather duties approximated 30 per cent, except for those reductions under the Compromise Act, until 1842. Tariff rates on leather were then changed to six cents a pound for sole and common leather and eight cents for upper leather. These rates were revised in 1846 and placed on a 20 per cent ad valorem basis; at the same time a duty of five per cent was placed on hides and skins. This was the first duty placed on hides, a raw material in which the country was deficient in supply. In 1856 this duty was reduced to four per cent and the duty on leather lowered to 15 per cent. In 1862 a duty of 10 per cent was placed on raw hides and skins of all kinds.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: Rumpf Publishing Co., 1950.

In New England and New York during this [colonial] period, the principal material used for tanning was hemlock bark. In the central and southern colonies, oak bark was the principal material used. The southern states tanned only a part of their leather needs, buying the remainder from the north.

Ibid.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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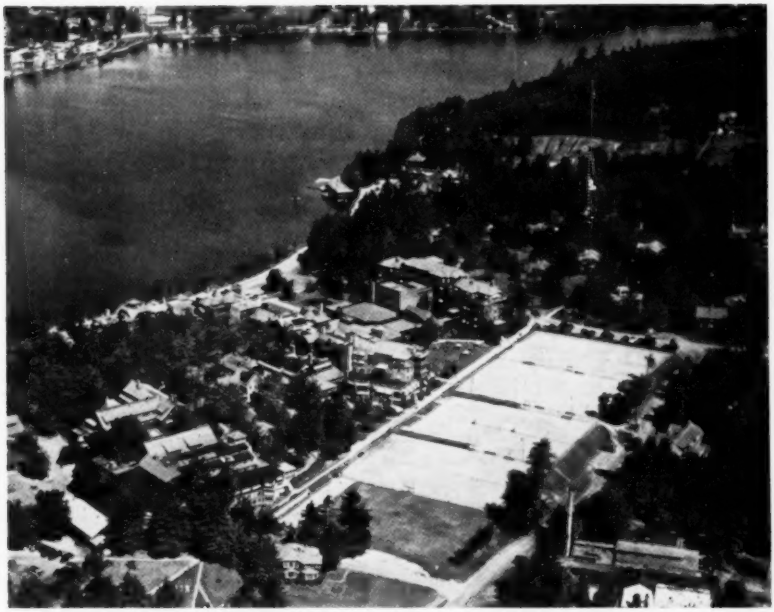
SPANISH ABSTRACTS

This issue initiates a policy of translating the abstracts of original papers into Spanish for the convenience of our many readers south of the border. The translations this month are the work of Jose Berliavsky, from Torreon, Coahuila, Mexico. Jose is now a second-year student in the Department of Leather Engineering at Lowell Technological Institute, Lowell, Mass.



LAKE PLACID CLUB—SITE OF 53rd ANNUAL MEETING

Air view of the main Clubhouse area and tennis courts. Mirror Lake in background. Plan now to attend the 53rd Annual Meeting here June 2–5, 1957.

THE COVER

The building pictured on this month's cover is familiar to many of our readers. It is the Research Laboratory of the Tanners' Council of America located at the University of Cincinnati.

The first leather research laboratory to be supported by the cooperative effort of the entire tanning industry of the United States was established in 1916 by the National Association of Tanners, predecessor of the Tanners' Council. When the directorship of that laboratory became vacant in 1921, the late George D. McLaughlin of the University of Cincinnati was offered the position. He accepted on condition that the laboratory be moved to Cincinnati. The present building was built by the Tanners' Council and given to the University in 1924.

The Laboratory is an integral part of the University where it forms the Department of Basic Science in Tanning Research of the Graduate School

of Arts and Sciences. Graduates of this department are found in all branches of the leather industry in this country and abroad.

The staff consists of the director, a physicist, and a biologist, as well as chemists. At present there are 30 staff members and 5 graduate students.

Operations of the Laboratory are supported by the industry, by military and other governmental agencies, and by individual contributors.

HOW CAN WE MAKE THE JOURNAL MORE USEFUL ?

The following letter raises important questions as to Journal policy, and makes a suggestion, well worth consideration, as to how the Journal can be made more useful.

Dear Dr. Merrill:

In discussing with some friends the activities of the ALCA and the potentialities of our organization, we came to the conclusion that besides the most important interest in research along scientific lines, an extension of our activities into the more practical field of our profession would be of great interest.

I would like to point in this connection to the increasing attention which is accorded to our round table discussion on practical tanning problems. However, this takes place only a few times a year and it surely is not in keeping with the need of our industry for the intelligent discussion of every-day practical problems.

Therefore, I would like to suggest adding to the Journal a new practical section, possibly under the heading "Open Forum", in which non-scientific problems could be discussed in the same manner as it is done in "Das Leder" under "Questions and Answers". I believe such a column would widen the interest in our Journal and make it more attractive to the practical men.

I would be very much interested to learn how you feel about such a suggestion.

Sincerely

Theordore D. Braunschweig

Jan. 13, 1957.

The editor is wholly in favor of any change or innovation that will make the Journal more useful to the Association, its members, and the leather industry. Comments on Mr. Braunschweig's suggestion are cordially invited. It must be understood that the Open Forum proposed by Mr. Braunschweig would have to depend on spontaneous, voluntary contributions, both as to questions asked and answers provided. According to the editor of *Das Leder*, his experience with the Question and Answer department has not been an altogether happy one.

—EDITOR

NECROLOGY

The deaths of three men prominent in the leather industry are announced with deep regret.

Dr. Paul Beer died January 16, 1957, while at work, at the age of 68. He was Managing Director of the Collis Leather Co., Ltd., and Vice-President and Managing Director of Beardmore and Co., Ltd., Acton, Ontario, Canada. A native of Budapest, he received his Doctorate from the University of Karlsruhe. Following active service in the first world war, during which he was severely wounded, he joined Mauthner Bros., Tanners, of Budapest, and remained with this firm until 1938, when he came to Canada on the invitation of the two companies with which he was associated for the rest of his life.

Dr. Joseph Caspe, an active member in our Association since 1930, passed away on October 22, 1956, in New York. He had returned from Trinidad where he was in the process of setting up a new factory.

Dr. Caspe was affiliated with Joseph Caspe, Inc., 50 Columbia Street, Newark, New Jersey, before moving to San Diego, California.

Dr. William R. Cox, an active member and chairman of the Raw Stock Committee, died of a heart attack on January 18, 1957. Services were held January 21 at the St. James Episcopal Church in Montclair, New Jersey.

William "Bill" Cox was born in Chicago in 1915 and came from a family of tanners. A graduate of West Orange High School and the Newark College of Engineering, he received his M.S. degree from Stevens Institute of Technology and his Ph.D degree in 1950 from the Graduate School of Arts and Sciences, University of Cincinnati.

Associated with New Jersey Tanning Company, Inc. until 1950, he then joined Seton Leather Company. At the time of his death, he was Assistant Secretary of that company and in charge of hide purchase and statistical quality control in the tannery.

Dr. Cox was a member of the American Chemical Society and Sigma Xi Honorary Scientific Fraternity. He served as a trustee of the Youth Consultation Service in Newark.

Dr. Cox is survived by his wife, Mrs. Mary S. Cox, two daughters, Mary and Jane, and a sister, Miss Emily J. Cox. His passing has been felt by a large number of professional and executive members of the tanning industry.

NEW POSITION FOR DR. M. M. BALDWIN

Dr. Maynard M. Baldwin has been appointed a technical director at Battelle Institute, Columbus, Ohio. In this capacity, he will guide technical aspects of the Institute's extensive chemical research.

Dr. Baldwin's varied research interests have included wood products preservation, agricultural and pharmaceutical chemicals, coke oven by-products, and organic synthesis. An authority on derivatives of coal tar, lignite, and mineral oil, he also includes leather chemistry and preservation in his background of experience. His published papers and patents issued or pending are in these and related fields.

Dr. Baldwin was graduated from Whitman College with a B.S. in chemistry and received his Ph.D. from the University of Washington. He joined the Battelle staff in 1938 after having been associated with the School of Mineral Industries of the Pennsylvania State College.

One of the organizers of the Society of Industrial Microbiologists, Dr. Baldwin is a member also of the American Chemical Society, the Chemists Club (New York City), and the American Leather Chemists Association. He is the present chairman of the subcommittee on research of the ALCA-ASTM Joint Committee on leather.

INTERNATIONAL LEATHER WEEK

PARIS, SEPTEMBER 7 – 12

The following cordial invitation has been received from the National Leather Association of France:

"The President and Council of the National Leather Association and the members of the Executive Committee of Leather Week present their best wishes and are pleased to welcome you to the International Week of Leather, which will take place September 7–12, 1957."

Since International Leather Week precedes the Rome meeting of the I.U.L.C.S. by only a few days, it is quite likely that some of our members who will attend the meeting of the International Union may arrange their itineraries so as to be in Paris during the week of September 7–12.

EMPLOYMENT NOTICE

WANTED—Position by member, 46 years old. Varied experience in laboratory and production. Heavy experience on demonstrations and sales of specialty products for tannery use. Considerable managerial experience. Highest references available from both tanning and chemical industries. Please reply to Box A-3-1, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

EDITORIAL

The article "English Style in Scientific Papers" by Professor John R. Baker (reprinted in last month's Journal) has aroused considerable interest and evoked some criticism. Personally, we discount Professor Baker's suggestion that the "German-American" style in scientific prose is "the product of childhood, introduced by people whose parents had spoken in sentences constructed in their native, German way." It seems to us much more likely that it is a matter of scientific, rather than biological, ancestry. From about 1880 to 1910, almost every top-grade American chemist did post-graduate work in Germany, wrote his first paper in German, and diligently read the *Berichte* and an assortment of *Zeitschriften*. Returning to a professorship in an American university, he continued to write papers in the style to which he had become accustomed. His students, consciously or otherwise, copied his style. *Their* students did the same.

Regardless of cause, however, Professor Baker is right in condemning this "Germanoid" style and calling for greater clarity of construction in our technical prose.

Letters from our readers on this subject would be most welcome.

—EDITOR

COUNCIL MEETING MINUTES

JANUARY 11, 1957

Plankinton House
Milwaukee, Wisconsin

A meeting of Council was called to order by President E. B. Thorstensen at the Plankinton House at 9:30 A.M., with all officers and Council members present. Also attending were Messrs. Turley, Wederbrand, Retzsch and Presley.

The minutes of the meeting held October 10, 1956 in Washington, D. C. were approved.

Mr. Maeser reported for the Technical Committees. A copy of this report is attached as Appendage I.

In consequence to this report:

Council approved the recommendation that after the 1957 annual meeting an errata flyleaf be prepared, published, and distributed to all members, giving the status of all methods at that time.

Council approved the suggested plan to label the Method B1 as published on page 496 of the September Journal, 1956, as B without any number, and

to leave Methods B1, 2, 3, 4 as they are now numbered, but when the minor detail changes as recommended by the committee and as published on pages 498, 499, 500, 501, 502 are made, to have new copies printed and distributed to all members.

It was reported that Hide Powder Lot No. 28 has been approved by the committee and is now offered for sale.

Upon recommendation of Chairman J. Wagoner, the Committee on Tannery Practice was dropped by motion of Dr. Compton, seconded by Mr. Weldon, unanimously approved by Council.

Council then requested Mr. Maeser to organize an Advisory Committee on Tannery Waste Disposal with Mr. Wagoner as chairman.

Upon motion by Mr. Maeser, seconded by Dr. Compton, Council unanimously approved the appointment of Merrill Leach to replace R. M. Koppenhoefer as chairman of the Fats and Oils Subcommittee of the Preparatory and Posttanning Processes Committee.

ASTM-ALCA Committee.—Mr. Maeser presented the following organization of the committee by Dr. Compton who has succeeded Mr. Maeser as chairman of the Physical and Mechanical Properties of Leather Committee.

The Physical and Mechanical Properties Committee has been organized as had been proposed at the Council meeting October 10. There are no subcommittees but most of the Committee members are chairmen of committees or sections of the ALCA-ASTM Joint Committee on Leather. A list of the Committee members and their ALCA-ASTM Joint Committee responsibilities follows:

Name	*Responsibility*
R. J. Ashcraft, Subcommittee III	Effect of water
M. Baldwin, Chairman, Subcommittee IV	Research
G. A. Butz, Chairman, Subcommittee III	General physical testing
A. N. Compton, Chairman, Subcommittee III, Section VII	Mechanical leathers
J. R. Kanagy, Chairman, ALCA-ASTM Joint Committee	
Arthur Kay, Chairman, Subcommittee III, Section X	Miscellaneous physical properties
R. M. Lollar, Chairman, Subcommittee I	Nomenclature, definitions, and applicability

Name	*Responsibility*
C. W. MANN, Chairman, Subcommittee II	Sampling and conditions for physical testing
J. NAGHSI, Chairman, Subcommittee III, Section II	Physical dimensions
J. S. ROGERS	
W. T. RODDY	
R. STUBBINGS, Chairman, Subcommittee III, Section V	Surface characteristics
R. YOUNG, Chairman, Subcommittee III, Section III	Tensile properties

A motion to approve this organization was made by Mr. Maeser, seconded by Dr. Stubbings, and unanimously passed. It was the opinion of Council that a person serving on the ALCA-ASTM Committee and the ALCA Committee was acceptable.

A suggestion was made by Mr. Maeser that chairmen of all Technical Committees be requested to give a report on their committee activities at the January meeting of Council, so that such reports can be studied, approved, and published before the annual meeting. Upon motion by Dr. Compton, seconded by Dr. Stubbings, this suggestion was unanimously approved by Council. Such a plan is to become effective January, 1958.

Method J40, Sampling of Tannery Chemicals, as prepared by Mr. Roddy and approved by Mr. Maeser, was approved by Council and ordered published as provisional and distributed to members.

Mr. Maeser reviewed the need for work on the interpretation of methods results and the validity of the present sampling requirements. Council was sympathetic to the suggestion and asked Mr. Maeser to submit in greater detail what he had in mind and what cost would be concerned, at the next meeting.

Convention Committee.—Mr. Clinton Retzsch presented the following organization of his committee and proposed budget for the 1957 meeting:

COMMITTEE MEMBERS

Chairman	C. E. RETZSCH
Vice Chairman	R. STUBBINGS
Entertainment	J. CASNOCHA and F. KLIMPL
Hotel and Transportation	H. BERNARD
Golf	M. LINDSAY and W. HAMMELL
Publicity	J. STELLMACH
Ladies' Activities	MRS. H. BERNARD

PROPOSED AGENDA

Sunday, June 2

Council Meeting
Committee Meetings
President's Reception

Monday, June 3

A.M.	Technical Papers
P.M.	Golf Tournament
Evening	Dinner Dance

Tuesday, June 4

A.M.	Technical Papers
P.M.	Technical Papers
Evening	Banquet

Wednesday, June 5

A.M.	Tanning Symposium
P.M.	Council Meeting

PROPOSED BUDGET

Receipts

Student Registration—$1.00 not inc. banquet	
Member Registration—300 @ $6.00	$1,800.00
Guest Registration—50 @ $12.00	600.00
Display Rental (less 10% to hotel)	1,000.00
	$3,400.00

Expenditures

Registration	$ 250.00
Transcription	550.00
Public Address, Slides, etc.	100.00
Social and Entertainment	1,700.00
Golf Tournament	350.00
Ladies' Activities	300.00
	$3,250.00

Upon motion by Mr. Maeser, seconded by Dr. Compton, Council approved the committee organization and a budget not to exceed $3600.00.

Mr. Retzsch then proposed that a letter be sent to each member soliciting papers with a deadline for abstracts set as February 28. Council directed the

Secretary to send out such letter to all members at once. Mr. Retzsch is to write a personal letter to a selected list of persons. Council members were asked to use every effort to solicit papers.

Ways and Means Committee.—Mr. Wederbrand presented the following budget for 1957. Upon motion by Mr. Maeser, seconded by Dr. Compton, Council approved this budget.

BUDGET FOR 1957

	1956 Proposed	1956 Actual	1957 Proposed
General Account: Income			
Dues	$11,500.00	$11,489.01	$11,500.00
Interest on United States Bonds	1,100.00	1,075.00*	1,100.00
Methods	100.00	82.57	20.00
Annual Meeting	–0–	–0–	–0–
Directory	800.00	804.20	800.00
Total	$13,500.00	$13,450.78	$13,420.00
General Account: Expense			
Executive Secretary's Office	$ 4,200.00	$ 4,200.00	$ 4,600.00
Secretary's Office Expense	1,000.00	1,380.44*	1,200.00
Annual Meeting	400.00	218.07	400.00
Committee Work	100.00	109.25	100.00
Council Meeting	100.00	84.35	100.00
Audit	175.00	200.00	200.00
Printing of Methods & By-Laws	500.00	361.35	400.00
Printing of Directory	900.00	912.19	925.00
Reserve for Uncollectible Accounts	300.00	476.00	400.00
Winheim Award	–0–	–0–	100.00
Total	$ 7,675.00	$ 7,941.65	$ 8,425.00
Surplus on General Accounts	$ 5,825.00	$ 5,509.13	$ 4,995.00
Journal Account: Income			
Advertisements	$12,000.00	$11,348.19	$11,500.00
Subscriptions	5,200.00	5,372.88	5,400.00
Journals, Volumes, Reprints	2,400.00	2,496.19	2,400.00
Dues, S.L.T.C., Difference	950.00	806.00	800.00
Total	$20,550.00	$20,023.26	$20,100.00
Journal Account: Expense			
Printing & Publishing	$17,000.00	$18,082.43	$18,000.00
Printing Reprints	2,400.00	1,640.00	2,400.00
Copyright, Insurance, Storage	500.00	520.00	500.00

*Estimated amount.

	1956 Proposed	1956 Actual	1957 Proposed
Abstracts & Translations	400.00	305.00	400.00
Editor's Salary	500.00	350.00	–0–
Editor's Office Expense	–0–	57.70	–0–
Editor-in-Chief's Salary	600.00	500.00	600.00
Editor-in-Chief's Office Expense	400.00	358.38	400.00
Managing Editor's Salary	2,500.00	2,083.33	2,500.00
Managing Editor's Office Expense	300.00	120.35	300.00
Advertising Discount Allowed	150.00	123.57	150.00
Total	$24,750.00	$24,140.76	$25,250.00
Deficit on Journal Account	$ 4,200.00	$ 4,117.50	$ 5,150.00
Difference	$ 1,625.00 (Surplus)	$ 1,391.63 (Surplus)	$ 155.00 (Deficit)

Mr. Wederbrand reported that he had ten subscribers for exhibit booths.

Nomination Committee.—Mr. Arthur Kay, Chairman of the Nominating Committee, presented the following report:

"*To Officers and Council*:

"The Nominating Committee has selected the following candidates for office of ordinary members of Council. Each nominee has agreed to serve if elected.

DAVID BALFOUR
HAROLD R. MILLER, JR.
HARRY J. WIDNEY
CHARLES A. MARTIN
HERBERT A. TETREAULT
C. DAVID WILSON

"The committee having served its purpose asks to be discharged, and the chairman expresses his appreciation to the members of the committee.

"A. N. KAY, *Chairman*
DOMINIC MEO
REUBEN HENRICH"

Papers for International Union of Leather Chemists Societies Meeting.—A total of five papers were submitted in abstract to the Secretary of the ALCA. These were submitted to Mr. Weldon, chairman of the committee appointed to make the award. The Secretary was instructed to acknowledge the papers and advise each person that the complete paper must be submitted by March 1, 1957.

Renewal Announcement.—Council approved the insertion of a flysheet in the December issue each year calling attention to the dues and subscriptions being payable as of January 1.

International Union of Leather Chemists Societies.—A letter from Dr. A. Harvey, Hon. General Secretary of International Union of Leather Chemists Societies, was submitted to Council in which the Yugoslav Society petitioned membership in the Union. Upon motion made and seconded, Council unanimously approved acceptance and the Secretary was instructed to so inform Dr. Harvey.

Dr. Harvey also wrote that at the meeting in September, 1957, a symposium on Leather Making would be part of the meeting. The ALCA was asked to designate the subject which they would discuss. Dr. Turley, now President of the International Union, spoke on this subject as well as the general program. It was agreed that the ALCA delegate would discuss chrome tanning. Council, upon a motion duly made and seconded, unanimously approved this plan and appointed President Thorstensen to make the presentation.

New Members.—The following persons were elected to active membership:

JOHN G. ROONEY
RAYMOND A. HAUCK

The following members were elected from associate to active membership status:

MILTON BAILEY
LUCIEN BUCK

The following person was elected to associate membership:

THOMAS L. DORRIAN

Membership.—A list of members who have not paid their dues was read. The Secretary was instructed to send a copy of this list to each member of Council, and each person is to see if he can get these members to come back, pay their dues, and assume membership.

Deceased Members.—The following list of members deceased in 1956 was read:

WILLIAM Z. BEIER
AUGUST BOSS
JOHN M. COYLE
W. P. FRITZ
FRED L. HILBERT
ELLIS B. MILLER
GEORGE MOSBAUGH
CURTIS PETERSON

President Thorstensen appointed the following members to a committee to prepare a resolution for presentation to Dr. R. M. Koppenhoefer for the fine services he has rendered to the Association and well wishes for success and happiness in his new position:

E. D. COMPTON
ROBERT STUBBINGS
FRED O'FLAHERTY

Biographical Data.—President Thorstensen reported that after much study regarding the best way to file the biographical data on members, it was decided to use loose-leaf books and index the capabilities, interests, and records of members. The Secretary's office is to do this.

Student Members' Registration.—Council approved a registration fee for students attending the annual meeting of $1.00. This is not to include the presidential reception or the banquet.

Delegates to International Meeting.—Upon motion by Mr. Maeser, seconded by Dr. Stubbings, Council delegated to the President the authority to appoint such persons as will attend the International Meeting as official delegates.

Upon motion made by Mr. Weldon, seconded by Dr. Compton, Council approved President Thorstensen and Secretary O'Flahery as official delegates and authorized a total sum of $1,000.00 to be furnished in defraying their expenses.

Perkin Centennial Publication.—The Secretary reported that Council by mail ballot voted not to contribute money to the Perkin Centennial Committee to defray the cost of publishing the paper presented by Dr. Stubbings.

Dr. Compton reported that the Centennial Committee had agreed to defray such expenses and that all papers will be published.

Editor's Report.—A meeting was held by Editor Merrill and his board, and he made the following recommendations which are contained in his report, Appendage II:

That Dr. Thomas Thorstensen be appointed Associate Editor for the next two years, to serve without compensation; and

That Mr. Earl J. Watt be contracted to serve as Managing Editor for the next two years.

These matters were discussed with each member of Council and unanimously approved.

The Secretary was instructed to prepare an agreement to be signed by President Thorstensen representing the ALCA and Mr. Watt.

There being no further business the meeting adjourned.

Respectfully submitted,

FRED O'FLAHERTY
Secretary

APPENDAGE I

REPORT OF THE TECHNICAL COMMITTEES

The Coordinator of Technical Committee activities wishes to bring the following matters to the attention of the Council.

1. Tannery Practice Committee.—Mr. J. Wagoner suggests that the Tannery Practice Committee is not functioning as such. Most of the problems which they might undertake are problems for management and are not within the province of the ALCA. He suggests that the committee be disbanded and that a committee on Tannery Waste Disposal be formed to function as a clearinghouse for gathering and dispensing information on the subject.

2. Preparatory and Posttanning Committee.

Fats and Oils Subcommittee.—Dr. Robert Koppenhoefer has found it necessary to resign as chairman of this subcommittee. He suggests, and W. Roddy agrees to, the appointment of Merrill Leach to the chairmanship.

3. Hide Powder Committee.—I. D. Clarke reports that Hide Powder Lot No. 28 has been approved by his committee and Frank Marshall has been authorized to sell it.

4. Committee Reports.—It has been customary for the Coordinator of Technical Committees to secure a report from each committee chairman prior to each Council meeting. A report of the actions taken by the committees at the meeting on Sunday preceding the Convention is generally made to the members at the Annual Meeting on Tuesday. This rushes matters so that it is difficult to properly present committee matters to the membership.

It is suggested that only one committee report be made each year and that the report be submitted by the committee chairmen to the Coordinator of Committees not later than December 1 of each year. This will give ample time (1) for the chairmen to report properly the actions taken by the committees at and following their meeting at the Convention and (2) for the Coordinator of Committees to present the committee work to the Council at the January meeting in a clear and meaningful manner. If, following Council approval of committee recommendations, action by the membership is required on any matters such as approval of new methods or changing the status of old methods, there will be time for publication of such matters in the Journal, and a proper presentation to the membership can be made at the Annual Meeting.

5. Sampling and Methods Evaluation.—Because leather is so variable from one skin position to another, from one skin to another, and due to the direction of cutting, the users of test methods are constantly faced with the problems of proper sampling and evaluation of the test results. These prob-

lems are much more difficult in testing leather than in testing other manufactured materials.

Because of this wide variability, simple sampling, simple test procedures, and evaluation of data based on numerical averages will not, in general, give dependable and useful results. If useful results are to be obtained, methods for sampling, testing, and the evaluation of results which are statistically acceptable, will have to be found.

Such work generally consists of two parts: (1) setting up on the test plan both sampling and test procedures and the method of analysis to be used in evaluating the results, and (2) the time-consuming and often tedious work of running the tests and performing the necessary calculations on the results.

There are, in our Association, only a limited number of men with the background and training to perform the first function. They are all busy with their regular work but would, in general, be willing to give the time necessary to set up and oversee the problem. It would, however, be a distinct imposition to expect such men to carry out the time-consuming routine function noted in part 2. It is suggested that the Council consider appropriating a certain amount of money to be used to pay for such help.

It is recognized that this suggestion breaks a long-established precedent of this and other technical associations, which dictates that technical committees perform their functions without any substantial financial support from the association. Acceptance of this proposal may open the door to demands of other technical groups for support by the Association and have other side effects which could prove to be either costly or bad.

It is hoped that Council will discuss this matter at this meeting but withhold any action regarding it until at least the next Council meeting. In the meantime, the suggestion can be discussed and carefully considered before any action is taken.

M. MAESER
President-Elect

APPENDAGE II

REPORT OF THE EDITOR-IN-CHIEF FOR 1956

Mr. Watt, the Managing Editor, and I did not assume our duties until March 1, 1956. The first four numbers, January through April, were edited by R. H. Twining as Acting Editor. The Association is much indebted to Mr. Twining for the able services that he rendered for more than six months following the death of Editor Dean Williams. I wish to acknowledge my great personal obligation to Mr. Twining for his help and cooperation when the new editorial plan was put into effect.

In 1956, the Journal published 745 pages, including indexes but excluding advertisements, distributed as follows:

	Number	Pages
Papers, addresses, technical reports	43	445
Abstracts, including patents	323	109
Book notices and reviews	15	6
News items, notices, reports, and miscellaneous	—	114
Title pages and indexes		71
Total		745

Our chief problem continues to be a shortage of original papers. As of January 1, 1957, after providing for the first two issues of 1957, we had on hand only four manuscripts, in various stages of editing. Three papers presented at the 1956 meeting (and one from the 1955 meeting) have not yet been submitted for publication. An encouraging factor is the number of papers received from laboratories outside the United States. Six of the papers published in 1956 came from overseas, and four more foreign contributions have been accepted or are being reviewed. These contributions from India, South Africa, and Latin America are most welcome, and I hope to get more of them.

The coverage of the abstract section has been broadened, though much remains to be done on that score, and a number of new abstracters have joined the faithful group who have served the Journal for years.

The Editorial Board has been enlarged and strengthened, and is playing an active role in the editing of the Journal. As a rule, each manuscript that I receive is referred to a member of the board who is familiar with the subject matter for an opinion as to its acceptability, and for suggestions as to how the paper might be improved. This procedure has served to eliminate a good many mistakes and ambiguities in manuscripts before they are published, and seems to be welcomed rather than resented by our contributors. I wish to thank all members of the Board for their help and cooperation.

The need for an Associate Editor, who will be prepared to take over the duties of the Editor-in-Chief in case the latter should be incapacitated, has been called to the Council's attention previously. With the approval of the Editorial Board, I recommend Dr. Thomas C. Thorstensen for this position. It is understood that this appointment carries no implications as to who my successor will be when my term expires.

The arrangement whereby the duties of editing the Journal are split between a Managing Editor and an Editor-in-Chief, which the Council approved in January, 1956, for a one-year trial, has worked excellently. Mr. Watt and myself have worked together in complete harmony. Nearly all the changes that have been made in arrangement and typography, and the

introduction of other features intended to make the Journal more interesting were suggested by Mr. Watt. Practically all the comments on these changes that I have heard have been highly favorable. I recommend that the contract with Mr. Watt be renewed for two years more.

H. B. MERRILL
Editor-in-Chief

The first tannery recorded in New Jersey was at Elizabethtown in 1660. It is interesting to note that this was perhaps the first tannery to manufacture leather for other than its immediate community. With plenty of hides and bark available, leather was produced and shipped to the New York market.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: The Rumpf Publishing Company, 1950.

A fundamental contribution to the development of tanning machinery was made in 1878 and new developments in tannery drying equipment were foreshadowed when Sturtevant began work on blowers and suction fans.

Ibid.

In 1905 more sole leather was exported from the United States than from all other leather-producing countries combined.

Ibid.

In 1952, thirty-two colleges and universities reported 14,000 people on their staffs employed full-time and part-time on government research, and that the percentage of government-contract employees in these institutions ranged from a low of 1 to 2 percent to a high of more than 50 percent, the latter obviously in an institution operating a large specialized research center strictly on government work.

These figures do have meaning for us, however, in illustrating the tremendous demands for scientific personnel trained in colleges and universities, for work on problems *directly related to national security, for which the Federal Government clearly has primary if not almost exclusive responsibility.*

—Russell I. Thackrey, American Association of Land-Grant Colleges and Universities, in *The Strength to Meet Our National Need.* Washington, D. C.: American Council on Education, 1956.

Plans for the discovery and development of scientific talent must be related to the other needs of society for high ability; science, in the words of the man on the street, must not, and must not try to, hog it all. There is never enough ability at high levels to satisfy all the needs of the nation; we should not seek to draw into science any more of it than science's proportionate share.

—Vannevar Bush, *Science, The Endless Frontier.* Washington, D. C.: U. S. Govt. Printing Office, 1945.

ABSTRACTS

Evidence for the Presence of the—OH—O=C—Link in Collagen from Its Fixation of Nonionic Chromium Complexes. K. H. Gustavson. *Acta Chem. Scand.*, **9**, 1049–55 (1955) (in English); cf. *JALCA*, **51**, 676 (1956).—Fuller and more detailed evidence is presented. Hide powders, variously treated, and a modified polyamide were tanned with wattle extract and with a variety of Cr tanning agents, washed, and analyzed. The tanning time was 48 hr. except for wattle (1 week) and the oxalato-chromiate (2 weeks); the latter tans very slowly, perhaps because it is fixed mainly by some collagen groups that are released gradually from some form of cross-linking. A summary of results is given below:

TABLE I

Material Tanned and Pretreatment	Total N %	Meq. N-Acetyl	Meq. O-Acetyl	Acid-binding Capacity (Meq. HCl)	Shrink Temp. °C.
Hide Powder 1, no pretreatment	18.05	none	none	0.92	65
H.P. 2, heat-shrunk	18.0	none	none	0.92	—
H.P. 3, 2 *M* $NaClO_4$	—	—	—	—	—
H.P. 4, N-acetylation	17.9	0.39	none	0.76	66
H. P. 5, partial O-acetylation	17.2	0.39	1.01	0.72	44
H.P. 6, complete acetylation	16.6	0.39	1.25	0.60	40
H.P. 7, esterified	17.3	none	none	0.11	35

TABLE II

Material Tanned and Pretreatment	Tanning Agents (*grams fixed per 100 g. hide substance*)								
	A	B	C	D	E	F	G	H	I
Polyamide	97	0.2	0.3	2.5	7.2	0.2	0.9	4.5	0.1
Hide Powder 1, no pretreatment	60	10.2	6.6	12.4	8.4	23.9	29.4	17.2	6.7
H.P. 2, heat-shrunk	96	11.0	8.8	18.1	14.1	37.0	53.8	27.5	12.4
H.P. 3, 2 *M* $NaClO_4$	118	11.9	6.2	21.3	15.9	40.7	60.3	30.4	13.9
H.P. 4, N-acetylation	56	8.2	6.5	11.2	7.7	19.2	25.8	15.2	5.9
H.P. 5, partial O-acetylation	78	7.8	7.6	15.5	10.0	—	24.1	—	—
H.P. 6, complete acetylation	93	7.0	7.8	18.7	12.4	20.8	22.7	15.8	5.1
H.P. 7, esterified	124	0.1	0.4	3.1	2.6	21.0	40.6	7.0	13.6

TANNING AGENTS

A — Wattle extract

B — Cr sulfate, 67% acid, 0.4 *N*, 98% cationic

C — Cr chloride, 67% acid, 1 *N*, mainly cationic

D — Cr chloride, 33% acid, 0.6 *N*, 30% cationic, 70% nonionic

E — Cr perchlorate, 33% acid, 0.6 *N*, 32% cationic, 68% anionic

F — Cr sulfate, 67% acid, 0.8 *N*, Plus 2 Na_2SO_3: 1 Cr_2O_3, 12% cationic, 80% nonionic, 8% anionic

G — Same, 2.5 Na_2SO_3: 1 Cr_2O_3, 86% nonionic, 14% anionic

H — Same, 1 Na phthalate: 1 Cr_2O_3, 35% cationic, 65% nonionic, highly aggregated

I — Tetraoxalato-diol-chromiate, 0.8 *N*, wholly anionic

The polyamide contains only peptide (–NH–C=O) links. Wattle tannin combines chiefly by H-bonding with peptide groups. The large increase in fixation of wattle by Hide Powders 2, 3, and 7 compared to 1 is due to disruption of cross-links between peptide groups during the pretreatments. Sulfite-masked Cr liquor apparently is not fixed by peptide groups, because it does not combine with polyamide; this is not due to lack of penetration, because the more highly aggregated phthalate-masked Cr liquor is fixed by polyamide. Nevertheless, rupture of cross-links involving peptide groups of collagen, as in Hide Powders 2 and 3, brings about a very large increase in Cr fixation from sulfite-masked liquor, while blocking of OH groups by acetylation (Hide Powders 6 and 7) causes the Cr fixation to be less than in normal hide powder. It is inferred that the increased fixation of Cr from sulfite-masked liquor is due to rupture of cross-links between peptide groups and hydroxyls, the freeing of the latter being responsible for the increased fixation. H.B.M.

The Spanish Chestnut in Europe. R. Sormani. *Das Leder*, **7**, 229–33 (1956).—Chestnuts (*Castanea sativa* or *C. vesca*) have been cultivated for their edible nuts from early times. They are susceptible to the ink disease (*Blepharosphora cambivora*) and to the blight (bark canker, *Endothia parasitica*), but are less susceptible to blight than the American chestnut. European stands in thousands of hectares are as follows: Italy 730, France 450, Spain 111, Portugal 80, Yugoslavia 60, Switzerland 17. The wood contains approximately 8% tannin. Trees should be over 70 years old when cut and the logs should be stored for 2 years to reduce the moisture content from 50% to 40% before extraction. Types of commercial extract are: liquid (34% tannin), solid (67%), powdered (ground, solid, 71%), and powdered, spray-dried (80%). In 1952 in Italy, France, and Switzerland 63,000 tons of extract (100% tannin basis) were made. Both "natural", (pH 3.5) and "neutralized" (pH 4.5) extracts are manufactured. The uses of chestnut extract are discussed. I.D.C.

Change in Strength of Chrome Leather by Retannage. B. Zorn. *Das Leder*, **7**, 193–98 (1956).—Chrome side leather (*A*) and goatskin leather (*B*) were retanned with the following 3 materials: (1) a resin tanning agent (Retigan R6, Bayer), using 4% on *A* and 6% on *B*; (2) a syntan, 4% of solid Tanigan extra special Pl for *A* and 6% of Tanigan extra Q+B for *B*; and (3) vegetable tannin, 4% (tannin basis) sweetened chestnut for *A* and 6% wattle for *B*. The leathers were fatliquored with 4.5–5% of sulfonated sperm oil

containing a little raw oil. The straight Cr leather, containing 30% less oil than the retanned leathers, was compared with the resin-retanned leather; the latter was compared with the other two retanned leathers. Preliminary tests were made to assure that opposite sides of a skin were comparable. All specimens were conditioned for 48 hours at 65% relative humidity and 19°–20°C. Increasing the fat content from 3.1% to 4.66% did not change tensile strength but increased stitch tear and split tear 11–15%. The tensile strength test is much used but means little except for belting and a few special types of leather; it is influenced by moisture and fat content of the leather, rate of test, direction of test specimen with respect to the backbone, etc. Relative strength (kg/cm^2) is of little value for comparisons as the treatment may change thickness. Retannage with resin or syntan increased the absolute strength by 5% but vegetable retannage lowered it 8–11%. Stitch tear of leather *A* was increased about 14% by resin or syntan retannage and decreased 8% by vegetable retannage but the tear strength of leather *B* was decreased by each retannage, 14% for the first two and 26% for vegetable. The split tear of *A* was increased a little by resin retannage but not changed by syntan or vegetable retannage. The split-tear strength of leather *B*, however, was decreased about 19% by resin and 32% by syntan or vegetable retannage. Burst tests were made, but the results of this test are difficult to evaluate. I.D.C.

Investigations on Opening up Fur Skins with Ammonium Salts and Enzymes instead of an Acid Pickle. H. Herfeld and S. Beyer. *Ges. Abhandl. Deut. Lederinst., Freiberg/Sa.*, **No. 13,** 69–91 (1956).—Previous work (see *JALCA*, **51,** 395 [1956]) showed that fur skins that were treated first with HCHO and then with ammonium salts, instead of the usual acid pickle, could not be shaved thin, but showed some desirable characteristics. Further tests on skins that do not need to be shaved very thin (goat, sheep, etc.) showed that the furs produced with the HCHO-ammonium salt process were at least equal to those produced with the acid pickle. The pretreatment with HCHO results in lessened solubilization of proteins, and the HCHO is not displaced as it is in the acid pickle. Best results were obtained with NH_4Cl; the sulfate gave too little opening up and the nitrate and thiocyanate too much. Tests were made with commercial mixtures of ammonium salts and enzymes sold for the pretreatment of furs. When these were used with HCOOH, as recommended by the vendors, very little more nitrogen was solubilized than with the equivalent amounts of ammonium salts only. The recommended procedure is to treat the soaked skins with 2% of HCHO (30%). After 3 hr. the pH is brought to 7.5–8.0 by adding Na_2CO_3. After 24 hr. the skins are washed and treated with 8–10% NH_4Cl for 2 days, then centrifuged, fatliquored, and finished as usual. Quantities are figured on the centrifuged skin weight. The float was 600%
H.B.M.

Leather Mildew Control. H. Bleemberg. *Leather and Shoes*, **132,** No. 23, 14 (1956).—A comparison is made between a stable derivative of ortho-phenylphenol and paranitrophenol. J.J.

The Mechanics of Leather. E. Petersen. *Shoe and Leather Reporter*, **284,** No. 5, 20 (1956).—The author gives a brief sketch of the cutting of hides into sides, the fleshing machine, unhairing, the tan drums, splitting, shaving, setting out, pasting, staking, buffing, and finishing operations. Suggestions are made

on how to overcome some of the defects experienced while operating tanning machinery and on controls that lead to better quality leather. J.J.

Spectrophotometric Studies in Leather Research. Y. Nayudamma, A. Nagasiromani, and D. Ramaswamy. *Bull. Central Leather Research Inst., Madras*, **2**, 29–43, 250–56 (1955/56).—The article opens with an excellent literature review, supplemented with 140 references, on the applications of spectrophotometry to the study of vegetable and mineral tannage problems. Original spectrophotometric data are presented on a number of Indian and imported conventional vegetable tanning materials. It was found possible to identify qualitatively the nature of these tanstuffs, to differentiate catechol from pyrogallol type tanstuffs, and to indicate promising substitutes for wattle. R.M.L.

Investigations on the Curing of Hides and Skins. S. C. Nandy, S. N. Sen, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **2**, 69–72, 237–49 (1955/56).—A fresh cowhide was salted with 35% common salt on the green weight and cut into portions on the third day after salting. These pieces contained 33.1% moisture and 19.5% NaCl. Water was added to individual pieces to give moisture contents ranging upward to 80%. Storage of all pieces in sealed jars at 34°C. for 8 weeks followed. The pieces were then analyzed for volatile and extractable nitrogen and bacterial count. The results indicated that deterioration did not occur below 40% moisture. Between 40 and 45% moisture, growth of microorganisms started to occur; while between 45 and 50% moisture, appreciable growth was noted. It is concluded that 45% moisture is the maximum permissible limit for efficient storage of wet-salted hides. A second portion of the work was concerned with the influence of humidity and temperature of storage during an 11-week period. While many factors related to the hide condition are involved, it is concluded that 80 to 70% R. H. is the most favorable for storage, and that 20° is a much better storage temperature than 30°C. The growth of halophilic bacteria was less apparent at the lower temperature. Hide moisture content of 45% was again affirmed as the maximum for safe storage. Limed hide weight yields were greater, when expressed on the cured weights, from the hide pieces stored under lower humidities. R.M.L.

Botanical Aspects of the Paper-Pulp and Tanning Industries in the United States—An Economic and Historical Survey. E. H. Fulling. *Am. J. Botany*, **43**, 621–34 (1956).—The rise and decline of vegetable tannin production in the U.S. is traced. H.B.M.

The Supercontraction of Wool in Lithium Bromide Solution. J. Griffith and A. E. Alexander. *Chemistry and Industry*, 1424–25 (1956).—Irreversible supercontraction of degreased wool ends, amounting to 50%, with a corresponding increase in diameter, was obtained with 8*M* LiBr at 100°C. in 3 hr. at pH 4 to 9. Some irregular results were traced to the presence of minute amounts of Br_2, which inhibited the supercontraction at 10^{-6} *M*. At $Br_2=10^{-5}$ *M*, the wool dissolved almost completely in 8*M* LiBr. Presence of detergents also interfered with supercontraction in some cases. H.B.M.

The Hydrochloric Acid-binding Capacity of Hide Powder in Sodium Chloride Solutions. P. M. Heertjes and Oei Hoo Djoen. *J. Soc. Leather Trades' Chemists*, **40,** 346–60 (1956).—The acid-binding power of Freiberg hide powder was determined by centrifuging the equilibrium-swollen material and weighing. Chloride ion was determined in the filtrate by Volhard's method, hydrogen ion by titration, acidity with a pH meter, and the quantity of peptized collagen by Kjeldahl procedure. Application of the Donnan theory showed that for NaCl concentrations of 1% or greater, the ratio between activities of dissolved Na, Cl, and H equal to unity. A method is described for calculation of the acid-binding properties of collagen as a function of pH. J.M.C.

Determination of Zirconium and/or Hafnium Using 1-Naphthylglycolic Acid. R. Hahn and P. Joseph. *Anal. Chem.*, **28,** 2019 (1956).—Both Zr and Hf are precipitated quantitatively from dilute acid solution by 1-naphthylglycolic acid. No interference is caused by Al, Fe(III), La, Sn(IV), Th, Ti, and UO_2 ions. The method was tested by the analysis of zircon ore. The results obtained using 1-naphthylglycolic acid compare favorably with those obtained with mendelic acid. Author's abstract

Recent Trends in the Analysis of Industrial Wastes. W. Moore and M. Ettinger. *Anal. Chem.*, **28,** 1819 (1956).—The rapidly expanding use of water for industrial purposes poses problems of employing the best analytical methods for critical evaluation and the control of industrial wastes. Development of methods of increased specificity and sensitivity beyond those employed in sewage disposal practice is required. Instrumental techniques, such as ultraviolet absorption, infrared absorption, X-ray diffraction of derivatives, and color reactions have been applied successfully to identify specific chemicals in industrial wastes. A critical re-examination of bio-assay and toxicological methods now in use is recommended in order to determine their suitability or adaptability to the increasing variety of industrial waste discharges and to reused surface waters. H.R.W.

Neutral Salt Effect in Semichrome Tanning: A Note. P. S. Ventkatachalam, Y. Nayudamma, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **2,** 257–58 (1956).—Vegetable-tanned leather was retanned with basic Cr sulfate solution to which was added different molar ratios, expressed on the basis of Cr_2O_3 used, of NaCl, Na_2SO_4, Na formate, K_2 oxalate, and Na_2 phthalate. A table shows the effect of the added salts on Cr fixation. Addition of NaCl and Na_2SO_4 reduces Cr fixation in the retannage of the vegetable leather, with the chloride having the greater effect. On the other hand, the organic acid salts increase fixation, unless the level of addition is too high. R.M.L.

Sulfation of Tobacco Seed Oil. V. R. Kishore. *Bull. Central Leather Research Inst., Madras*, **2,** 329 (1956).—The seeds of the tobacco plant yield 33 to 38% oil which is yellow and odorless. The oil is said to contain 16.2% oleic, 70.4% linoleic, 3.1% palmitic, and 4.8% stearic acid. A commercial sample of the oil gave I_2 value 119.2, acid value 4.5, and saponification value 187.4. Sulfated tobacco seed oil is a brownish-black, clear oil, giving a whitish, creamy emulsion with water at 1 to 10 concentration. Semichrome suedes were fatliquored with 3% of this sulfated oil on the weight of the leather with highly satisfactory results. J.J.

The Influence of Syntans on the Tanning Process. W. S. Short. *J. Soc. Leather Trades' Chemists*, **40**, 381–401 (1956).—The influence of syntans is considered in the light of their effects upon the colloidal properties of tannins and collagen. The conventional formulation for the basic phenolic syntan reaction, i.e., formation of a polymer consisting of phenol sulfonic acid monomers linked by methylene bridges, is criticized. An additional reaction involving formation of quinone-methides as intermediates with subsequent polymerization is suggested as the source of the true tannin components. A defense is given for the colloidal nature of concentrated natural tannin solutions. A certain critical tannin concentration must be exceeded for aggregation to occur. The influence of pH, by modifying the zeta-potential, can affect the physical state of tannins as well as the skin. Where natural tannin micelles are present in equilibrium with single tannin molecules, addition of syntan reduces micellar size. Where the tannin micelle is bound together with covalent bonds, the syntan increases stability of the tannin solution with particle size remaining constant. Addition of the syntan dinapthylmethane disulfonic acid to quebracho reduced insolubles from 38 to 1%. Pretreatment of hide by the same syntan resulted in increased rate of penetration of chestnut tannin. The chemical nature and practical application of amphoteric syntans are discussed.

J.M.C.

PATENTS

Making Leather; Tanning Furs. Brit. Pat. 755,331. Boehme Fettchemie Ges. Apl. Jan. 15, 1954.—Hides and skins are tanned and fatted by means of an aqueous emulsion comprising a non-sulphonated mineral, vegetable or animal oil, an inorganic tanning agent and a derivative of a water soluble polyalkylene oxide wax of molecular weight at least 2000. Conventional chrome tanning agents may be used, supplemented by common salt if desired. The non-sulphonated oil may for example be olein, train oils, tall oil, sperm oil or neat's foot oil. A cationic, anionic or non-ionic emulsifying or dispersing agent, or a mixture of any of these, or a precipitation product of reaction between an anionic and a cationic emulsifying or dispersing agent may be incorporated: in one example a cationic emulsifier prepared from octadecyl chloride and hexamethylene tetramine was used and in the other, an emulsifier prepared from oleyl alcohol and ethylene oxide. In addition a sodium alkyl sulphate paste was used in Example 1. The derivative of the polyalkylene oxide wax contains per molecule at least one aliphatic, cyclo-aliphatic, aliphatic-aromatic or aliphatic-cycloaliphatic hydrocarbon radical, having preferably at least four carbon atoms, united directly or indirectly to the terminal carbon atom or atoms of said wax through oxygen, sulphur or nitrogen, to which said terminal carbon atom or atoms is/are directly attached, preferably so as to produce as ester or amide derivative, emulsions and dispersions comprising derivatives of this kind wherein the molecular weight is 5000–10,000, being described and claimed in Specification 753,668. [*Group* III]. In the examples, a polyalkylene oxide esterified with stearic acid is used.

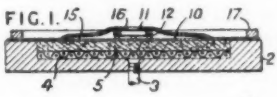
Process for Rendering Fibrous Material Water-repellent. U. S. Pat. 2,774,689. Ludwig Orthner and Martin Reuter, Frankfort am Main, Germany, assignors to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruning, Frankfurt am Main, Hochst, Germany, a company of Germany. Apl. Oct. 15, 1953.—The process of imparting hydrophobic properties to fibrous material which comprises treating the material with a solution in an organic solvent of a mixture of zirconium alcoholate and an organic acid selected from the group consisting of carboxylic and sulfinic acids.

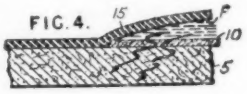
Water-repellent Treatment Utilizing a Methylhydrogenpolysiloxane and a Titanium Compound. U. S. Pat. 2,774,690. Sydney Russell Cockett, Halifax, John Gwynant Evans, Menston-in-Wharfedale, and George Landells, Leeds, England, assignors to Bradford Dyers' Association Limited, Bradford, England. Apl. April 8, 1952.—The method of rendering textile material water-repellent comprising contacting said material with both a methylhydrogenpolysiloxane containing between 1.0 and 1.5 methyl radicals and between 0.75 and 1.25 hydrogen atoms bonded to silicon per silicon atom, there being a total of between 2 and 2.25 methyl radicals plus hydrogen atoms per silicon atom, and a titanium compound selected from the group consisting of esters of titanic acid, titanium salts of fatty acids, titanium halides, and titanium sulfates.

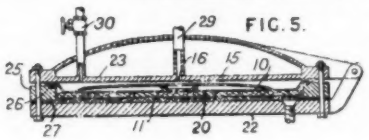
Tanning and Impregnating Leather; Waterproofing. Brit. Pat. 754,432. Highgate & Co., H. Apl. Oct. 1, 1953.—A single-step, dry process for producing soap comprises heating a mixture containing a fatty acid and a fatty alcohol, free or combined with one another, both the acid and the alcohol containing at least 14 carbon atoms, and an amount of solid anhydrous caustic alkali slightly in excess of that required to react with the free or combined fatty acid, to a temperature not appreciably in excess of 500° F., the mixture being stirred continuously until saponification of the fatty acid is completed, the fatty alcohol remaining substantially unchanged. The mixture may also contain mineral oil. A mixture containing a fatty acid, shark oil and/or sperm oil (which contain fatty alcohol) and a mineral oil may be saponified with anhydrous caustic soda, or a mixture of sperm oil and shark oil may be similarly saponified. Separately prepared fatty alcohols having straight or branched chains, e.g. cetyl, oleyl or stearyl alcohol, may be added to the saponification mixture. Such alcohols may be saturated or unsaturated, or unsaturated alcohols which have been hydrogenated. Sperm oil or shark oil used in the process may also be hydrogenated. The crude soap may be emulsified with oil, grease or wax and rubber latex. Leather may be impregnated with a soap-rubber latex emulsion and immersed in or drummed with a metallic salt solution to produce an insoluble soap, e.g. a lime soap, in situ, or the crude soap may be treated with mineral acids and then with ammonia to form an ammonium soap which is applied to leather in emulsion with rubber-latex; the leather is then heated to decompose the emulsion, the fatty acids so liberated acting with the rubber as a tanning agent. The leather may be treated to "cure" the rubber. Cloth may be treated with an emulsion of the soap with rubber latex and, after removing surplus emulsion, may be treated with aluminium acetate to obtain a waterproof effect. A soap-rubber latex may be incorporated into paper pulp to produce a waterproof paper. The soap may be boiled with mineral acids and from the product a mixture of fatty acids and alcohols may be extracted which may be used as an

emulsifying agent for oils, fats and waxes. A mixture of oil, acid and alcohol so produced may be neutralized with caustic soda, caustic potash, ammonia, triethanolamine or other base to provide jute-batching oils, fat-liquoring emulsions and waterproofing, binding or sizing agents. The Provisional Specification refers to Specification 470,715, [*Group* III].

Impregnating Porous Materials; Drying and Tanning Hides. Brit. Pat. 755,969. Secotan, Inc. Apl. Nov. 27, 1953.—An impregnating or treating fluid F, Fig. 4, is introduced between a permeable sheet such as a skin 10 to be







treated supported on a porous bed 5 of larger area, and an impervious membrane 15 overlying the sheet and bed and pressed against them by fluid pressure applied above the membrane or by applying suction to the under surface of the porous bed. The membrane is caused to seal selectively those regions of the bed not covered by the skin so that the treating fluid flows solely or mainly through the skin. The fluid introduced above the membrane to seal it selectively may be the fluid with which the skin is to be treated. The porous bed may be of wool felt, woven fabric, plaster of Paris, or ceramic material, and the membrane may be a sheet of rubber, polythene, or polyvinyl alcohol. As shown, a skin 10, Fig. 1, is placed on a porous bed of felt 5 laid on a screen 4 on a metal tray 2 with a drain connection 3. A spacer 11 in the form of a ring with downwardly extending legs 12 is placed on the skin, and a membrane 15 with a central hole 16 is placed over bed, skin, and spacer and held down by a rim member 17. Suction is applied at 3 to draw the membrane against the bed, and the treating fluid is introduced through the hole 16. If a buoyant membrane which will float on the treating liquid is used, the spacer may be dispensed with. In an alternative form. Fig. 5, a cover 23 is hinged to a base plate 22 carrying the porous bed 20, and a frame 25 provided with sealing gaskets 26, 27 forms with plate 22 and cover 23 a gas-tight enclosure. A skin 10 is placed on the bed 20 and a spacer 11 and membrane 15 with central hole 16 are superposed. When the cover 23 is lowered, the membrane is clamped between it and gasket 26. The liquid is introduced under pressure through a pipe 29 passing through the cover while air is vented through a valved pipe 30 until the whole space above the bed 20 is filled with liquid. On continued introduction of the liquid, the membrane seals the part of the bed 20 not covered by the membrane. Alternatively, air may be introduced through pipe 30 to cause the membrane to seal uncovered parts of the bed. The membrane may be secured to the cover about the inlet pipe 29 with the hole 16 surrounding the opening of the pipe. A pressure differential valve may be provided to hold the pressure difference in pipes 29 and 30 at a chosen value.

The apparatus may be used first to dehydrate a skin by treatment with acetone until the effluent is anhydrous, and then tan it with an ammonia-neutralized solution of chromic chloride in methanol and acetone.

Method of Removing Hair and Wool from Animal Hides and Skins. U. S. Pat. 2,775,504. Haskiel Zalcman, Braybrook, Victoria, Australia. Apl. April 14, 1951.—In the art of depilating lamb and sheep skins by applying a depilatory paint to the flesh side of the skins, the method of effecting depilation to obtain high quality wool while preserving the quality of the skin which consists in applying to the flesh side of the skin an aqueous composition which is substantially free of sources of monovalent metal cations and which comprises calcium hydrosulphide and lime, the calcium hydrosulphide being about 3 to 7% and the lime about 25 to 14%, each by weight of the composition, the proportion of calcium hydrosulphide decreasing and of lime increasing within the above ranges with the increasing thickness and fat content of the skin, the composition having a pH of not more than 12 and not less than about 11.7, and the source of hydroxyl ions being sufficient in quantity to provide an undissolved reserve thereof suspended in the composition; allowing the composition to remain on the skin until the wool is loosened, and then pulling the loosened wool from the skin.

Preparing and Treating Leather. Brit. Pat. 756,175. Farbenfabriken Bayer Akt.-Ges. Apl. Nov. 26, 1953.—Skins are impregnated, e.g. by milling in a hot-air drum before, during or after tanning with a mixture containing an aqueous polymerization emulsion of a compound containing at least one polymerizable double bond, at least 2 per cent (calculated on the weight of the polymer) of an anionic emulsifier containing a sulphonic acid group in the molecule, and a vegetable and/or synthetic tanning agent (specific vegetable tannins referred to are quebracho and mimosa, and "synthetic tanning agent" includes inorganic tannins such as chrome and purified sulphite waste liquors containing salts of lignin sulphonic acids and organic tannins such as a condensation product of naphthol sulphonic acids, phenol and formaldehyde or those described in Specifications 375,160, [*Group* IV], 443,967 and 496,898). Preferred polymerization emulsions are prepared from one or more vinyl compounds such as dichloroethene, vinyl chloride, an acrylic ester, styrene or acrylonitrile, if desired with minor proportions of one or more diene compounds. Substantial quantities of polymers with hydrophilic groups such as carboxyl should not be present. Suitable emulsifiers include sodium salts of alkylated naphthalene sulphonic acids and the sodium salts of long chain paraffin sulphonic acids, and the required quantity may be present during polymerization or made up thereafter. Polymerization is preferably carried out in neutral, acid or slightly alkaline medium. Preferred proportions of tannin and polymer lie between 1 : 1 and 1 : 5. In the examples: (1) leather is milled with a polymerization emulsion consisting of dichloroethene, butyl acrylate and the sodium salt of long chain sulphonic acids in the presence of a naphthol sulphonic acid/phenol-formaldehyde tanning agent; (2) chrome leather is milled with butadiene/acrylonitrile/styrene and an emulsifier according to Specification 678,614 and mimosa extract; (3) skins pretanned with (a) a mixture of the ammonium salt of a naphthalene sulphonic acid/formaldehyde and of a β-naphthol sulphonic acid/cresol/formaldehyde condensation product, or (b) chromium oxide, followed by neutralization, or (c) pretreated with sodium

chloride and hydrochloric acid followed by sodium thiosulphate to a pH of 5.2 to 5.4, and pretanned as in (a), are milled as in (1); (4) skins are pretanned with a mixture of the ammonium salt of a naphthalene sulphonic acid/formaldehyde and of a β-naphthol sulphonic acid/cresol/formaldehyde condensation product acidified with formic acid, a co-polymerization emulsion containing dichloroethene, butyl acrylate and the sodium salt of long chain sulphonic acids, and sodium thiosulphate, and then retanned and finished without the addition of fillers; (5) skins are pretreated with sodium thiosulphate and pretanned with the tannin used in (4) and then milled with a mixture of a co-polymerization emulsion containing butadiene, acrylonitrile and the sodium salt of long chain paraffin sulphonic acids and a naphthol sulphonic acid/phenol/formaldehyde condensation product; it is then tanned, retanned and finished; (6) leather is treated with a mixture of a co-polymerization emulsion containing dichloroethene, butyl acrylate and the sodium salt of long chain sulphonic acids, and a naphthol sulphonic acid/phenol/formaldehyde condensation product and finished without the addition of fillers. It is stated that the phenol tanning agent used in (1), (3), (5) and (6) could be used with a similar cresol tanning agent as in French Specification 897,222.

BOOK REVIEW

Colour Index. (2nd ed.) Compiled and published by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists (American address: Lowell Technological Institute, Lowell, Mass.). 4 Volumes, 3 parts. Volume 1, 1956.

Those who have used the 1924 edition of the *Colour Index* will welcome this long-awaited new edition. Actually, from the evidence in the first volume now being delivered one can conclude that this is a new, much more useful, almost encyclopedic work. The table of contents for the entire new *Colour Index* indicates that part I, in two volumes, will furnish information on commercial dyes and pigments classified according to their usage; that part II, which will comprise volume 3, will classify dyes and pigments according to their chemical constitution and will include an index of intermediates; and that the fourth volume, containing part III, will include the abbreviations index, fastness test data, a patents index, conversion tables, commercial names of dyes and pigments, a hue indication chart, and an appendix of additions and corrections. It is further the intent of the two sponsoring societies to issue supplemental volumes at intervals to keep this second edition up-to-date.

Volume 1 contains 809 large pages of text. A typical page includes information on two different dyes, giving application information, fastness properties, commercial designations of equivalent dyes, and industrial usage information. Dye types included are acid, mordant, basic, and disperse dyes and pigments. Food dyes and leather dyes are also specifically discussed in this volume. A special five-page index will make this volume especially useful to leather chemists, since every dye recommended for use on leather has been indexed under its hue classification.

Until May 1, 1957, the complete Index can be secured at a special advance price of $99; after this date the price may be advanced. This edition is highly recommended for all those concerned regularly with the dyeing of leather despite its high initial cost.

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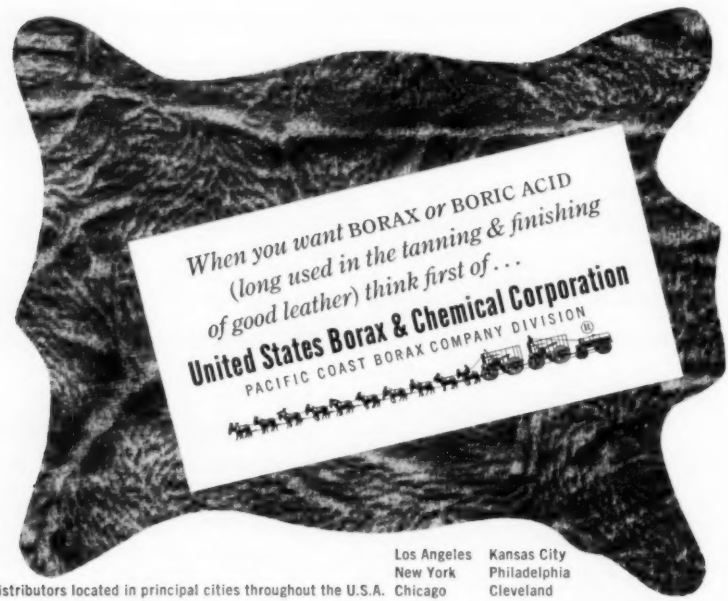
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